The Dynamic Stereochemistry of Some Dicarbonyl[phosphorus(III)](1,3-di-t-butyl-2-methoxyarene)chromium Compounds. Evidence for Restricted Rotation about Arene–Substituent Bonds, Including an *X*-Ray Crystal Structure of Dicarbonyl(triphenylphosphine)(1,3-di-t-butyl-2-methoxybenzene)chromium

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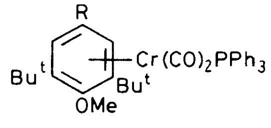
Low-temperature ^{1}H n.m.r. spectra of a series of dicarbonyl(triphenylphosphine)(1,3-di-t-butyl-2-methoxyarene)chromium compounds exhibit dynamic behaviour which is interpreted in terms of kinetic restriction of rotation about the arene–methoxy bond, and similar behaviour is observed in a chelated aryl chromium analogue of these compounds; this explanation is supported by an *X*-ray crystal structure of dicarbonyl(triphenylphosphine)(1,3-di-t-butyl-2-methoxybenzene)chromium in which the O–CH_3 group is *syn* to the chromium.

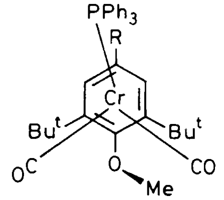
Solutions of dicarbonyl(triphenylphosphine)(1,3-di-t-butyl-2-methoxybenzene)chromium (**1**; R=H) and the corresponding 4-deuterio (**1**; R=D) and 4-methyl compounds (**1**; R=Me) show temperature-variable ^{1}H n.m.r. spectra. Spectra of the deuterio compound (**1**; R=D) in CD_2Cl_2 at temperatures below -50 °C showed doubling of signals for the methoxy group, the t-butyl groups, and the aromatic hydrogens. The signals were of unequal intensity within each pair of signals and the ratio of major to minor peak intensities was *ca.* 6:5. Spectra in $CDCl_3$ showed a different ratio in intensities (2:1) for the limiting low-temperature spectrum and the peak of higher intensity was at lower field for the methoxy and at higher field for the aromatic hydrogen signals, the reverse of the pattern of intensities shown for spectra recorded in CD_2Cl_2.

Theoretical spectra were calculated using the programme DNMR5 and assuming a two-site exchange from unequally occupied sites. Use of the calculated exchange rates in the Eyring equation gave values of $\Delta G^{\ddagger}$ of 47.2 and 48.1 kJ mol^{-1} in $CDCl_3$ and CD_2Cl_2 respectively. Similar values were obtained for the compounds with hydrogen and methyl replacing the deuterium atom at C-5. ^{13}C N.m.r. spectra of (**1**; R=H) were measured in CD_2Cl_2, but because of the low solubility of the compound it was not possible to measure spectra below -40 °C. At this temperature the methoxy carbon and C-1 signals had broadened extensively but other signals were unchanged. ^{1}H N.m.r. spectra of the tricarbonyl- and dicarbonyl-(triphenyl phosphite) compounds related to (**1**) were invariant in the temperature range 30 to -90 °C. Thus the free energy of activation of the dynamic process increases with the steric size of the substituents on the metal atom.

The *X*-ray crystal structure of (**1**; R=H) has been determined and is shown in Figure 1.[†] The conformation (**2**) with the two carbonyls eclipsing the t-butyl groups and with the triphenylphosphine residue over C-5 is preferred in the solid state. This eclipsing is surprising and in addition the O-methyl group was found to be on the same face of the aromatic ring as the chromium atom. The methyl group of the 2-methoxy group in tricarbonyl(1,2,3-trimethoxybenzene)chromium also adopts this conformation in the solid state.



(**1**)



(**2**)

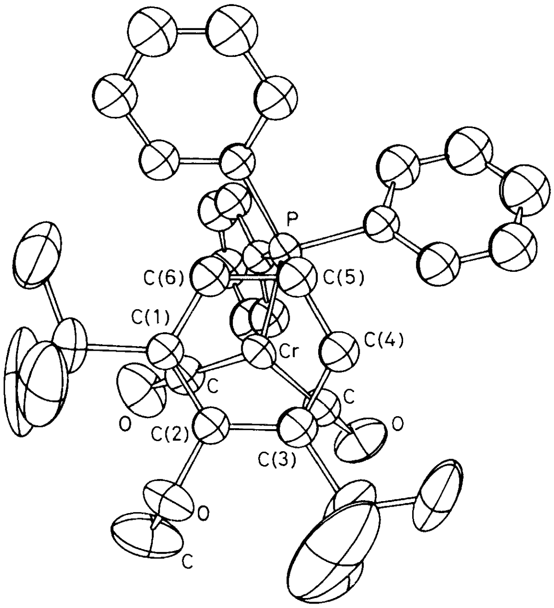
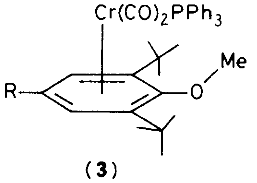
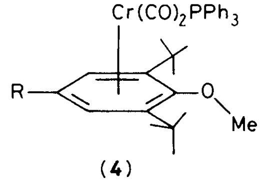


Figure 1. ORTEP diagram of compound (**1**; R=H) showing thermal ellipsoids at 50% probability level. The co-ordinated arene ring is in the plane of the paper and the chromium atom is behind this plane.



(**3**)



(**4**)

We believe that there are at least two possible explanations of the observed spectral behaviour. In the first the molecule freezes into the conformations (**3**) and (**4**) which differ in that the O-methyl group is restrained either on the same face of the arene ring as the metal atom (**3**) or on the opposite face (**4**). Previous work has shown that the barrier to rotation around

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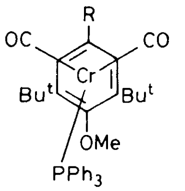
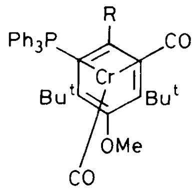
[†] *Crystal data:* diffraction data (Mo-K_{α}) for (**1**; R=H) were collected with a Philips PW1100 automated four-circle diffractometer and the structure solved by Patterson methods using the SHELX system; space group $P2_1/n$, $a = 21.236(9)$, $b = 13.729(9)$, $c = 11.023(8)$ Å, $\beta = 105.01(2)$; $D_c = 1.26$ g cm^{-3} for $M_r = 590.66$ and $Z = 4$. $R_F = 6.95\%$ ($R_{wF} = 6.51\%$) for 2612 reflections with $I > 3\sigma(I)$ and $6° < 2\theta < 60°$. Refinement was by full-matrix techniques with hydrogen atoms in calculated positions assuming C–H 1.08 Å.

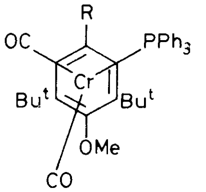
The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



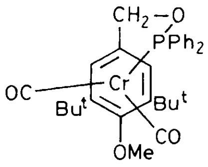
(5)



(6)



(7)



(8)

arene-α-substituent bonds is usually decreased by increasing the bulk of a metal-substituent on the arene ring as a result of a more severe increase in ground state rather than transition state interactions. Thus the free energies of activation for such processes are usually in the order: free ligand > ligand–$Cr(CO_3)$ > ligand–$Cr(CO)_2P(OPh)_3$ > ligand–$Cr(CO)_2PPh_3$. Examples include the barrier to rotation around the arene–C_α-bond in 1,2-dineopentyl-3,4,5,6-tetramethylbenzene which was lowered by 17.6 kJ mol^{-1} on complexing of the arene ring to a tricarbonylchromium residue.[2] In spite of this trend we believe that the observed dynamic n.m.r. spectra in (**1**) arise from kinetic restriction of rotation around the arene–oxygen bond. In conformation (**2**) the bulky triphenylphosphine group minimises adverse interactions with the t-butyl groups, and the O-methyl group is permitted to adopt either the *syn*- or *anti*-conformations shown in (**3**) or (**4**). With smaller ligands substituted on the metal this condition does not apply and dynamic spectra are not observed.

An alternative explanation is that rotation around the arene–chromium bond becomes kinetically restricted at low temperatures, freezing out the conformer (**5**) (which contains a mirror plane) and the two enantiomers (**6**) and (**7**). The enantiomers can rapidly interconvert by moving a CO past a t-butyl group so two sets of signals are observed, *viz.*, those of (**5**) and those of (**6**) and (**7**). This explanation was eliminated by low-temperature ^1H spectra of the cyclic compound (**8**). Spectra of (**8**) in CD_2Cl_2 and $C_6D_5CD_3$ showed similar dynamic behaviour to that of the non-cyclic compounds (**1**), with $\Delta G^\ddagger$ 49.7 kJ mol^{-1}. This chelate compound cannot adopt a conformation like (**5**) and there is no question of restricted rotation around the arene–chromium bond as a primary explanation of the observed phenomena. Significant barriers to rotation around arene–metal bonds have only been reported in the 'open-sandwich' compound (p-*t*-$BuC_6H_4Me)Ru(CO)(SiCl_3)_2$[3] and the 'closed-sandwich' compound (p-*t*-$BuC_6H_4Me)_2Cr$.[4] However, no evidence for restricted rotation was observed in ^1H n.m.r. spectra of dicarbonyl(triphenylphosphine)(1,3,5-tri-t-butylbenzene)chromium at temperatures down to −90 °C.[5] The recent claim of restricted rotation around the arene–chromium bond in dicarbonyl(hexaethylbenzene)thiocarbonylchromium[6] must thus be treated with great caution. In the cases reported here, it seems extremely unlikely that restricted arene-metal rotation is the reason for the observed dynamic n.m.r. spectral behaviour, and an explanation based on restricted arene–oxygen bond rotation is preferred.

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