The ^{13}C Nuclear Magnetic Resonance Spectra of the Complexes $[LM(CO)_3]$, L = Mesitylene, Durene, or Cycloheptatriene; M = Cr, Mo, W

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Summary The ^{13}C n.m.r. spectra of the complexes $[LM(CO)_3]$, (L = mesitylene, durene, or cycloheptatriene; M = Cr, Mo, W), and $^1J(^{183}W-^{13}CO)$ for [(durene) $W(CO)_3$] are reported and the ^{13}C chemical shifts are discussed.

THE application of ^{13}C n.m.r. spectroscopy to organic chemistry has been extensive and has yielded much interesting bonding information.[1] However, there has been a paucity of ^{13}C n.m.r. investigations of organometallic complexes, and there are no reports of the ^{13}C n.m.r. spectra of arenes or trienes bonded to metals. Thus the compounds $[LM(CO)_3]$, L = mesitylene, durene, or cycloheptatriene; M = Cr, Mo, W, have been examined and their ^{13}C n.m.r. chemical shifts are reported in the Table. For the tungsten complexes, $^1J(^{183}W–^{13}C)$ should be detectable, but on account of the low isotopic abundance of both ^{13}C and ^{183}W, $^1J(^{183}W–^{13}C)$ has only been detected for the carbonyls of $[(durene)\ W(CO)_3]$ where it is 189 ± 2 Hz.

^{13}C *n.m r. chemical shifts measured at 22·62 MHz in* CH_2Cl_2 *of mesitylene, durene, and cycloheptatriene and their complexes with* $M(CO)_3$, M = Cr, Mo, W. *The shifts (±0·1 p.p.m.) are relative to* Me_4Si *and increasing frequency is taken as being positive.*

	Free ligand, L		$[LM(CO)_3]$	
		M = Cr	Mo	W
(i) L = mesitylene				
$^{13}CH_3$	21·4	21·0	21·2	20·9
^{13}CH	127·6	92·4	94·7	90·9
^{13}CMe	138·6	111·5	111·7	111·1
^{13}CO	181·5[a]	235·1	223·7	212·6
(ii) L = durene				
$^{13}CH_3$	19·2	18·6	19·1	18·9
^{13}CH	131·6	99·0	101·4	97·3
^{13}CMe	134·4	107·6	118·8	107·9
^{13}CO	181·5[a]	235·5	224·4	213·7
(iii) L = cycloheptatriene				
$^{13}CH_2$	28·7	24·8	28·0	28·7
^{13}CH	121·3	57·6	61·3	52·3
^{13}CH	127·3	99·0	98·1	94·2
^{13}CH	131·3	101·9	103·7	101·7
^{13}CO	181·5[a]	232·7	220·6	211·6

[a] Calculated from R. Ettinger, P. Blume, A. Patterson, jun., and P. C. Lauterbur, *J. Chem. Phys.*, 1960, **33**, 1547. Measured as a gas at 8·5 MHz.

Grant *et al.* have interpreted the ^{13}C n.m.r. shifts in aromatic molecules by consideration of the mobile bond order at each carbon atom.[2] If it is assumed that changes in this term are dominant in determining the co-ordination shift when an unsaturated organic molecule is co-ordinated to a metal, then the co-ordination shift can readily be calculated from known C–C bond lengths. The C–C bond length in bis-(π-benzene)chromium[3] is 1·423 ± 0·002 Å and in hexamethylbenzenechromium tricarbonyl[4] is 1·42 Å, *i.e.* the bond length has increased from that of benzene 1·394 Å, to *ca.* that of graphite,[5] 1·4210 Å. Thus the co-ordinated arene has a mobile bond order of *ca.* 0·65 with a predicted co-ordination shift of *ca.* 26 p.p.m., in good agreement with the observed co-ordination shift. This treatment can be applied equally well to interpret the ^{13}C chemical shift of co-ordinated ethylene,[6] the π-allyl ligand,[7] co-ordinated dienes,[8] and the π-cyclopentadienyl ligand.[9]

In the case of the co-ordinated cycloheptatriene, assignment of the signals to individual carbon atoms has not yet proved possible. However, the average co-ordination shift, *ca.* 40 p.p.m., is considerably greater than that for the arenes, implying stronger metal–triene bonding than metal–arene bonding. Consistent with this view is that treatment of $Mo(CO)_6$ with 1-phenylcycloheptatriene does not give an arene complex, but the triene bonds to the metal.[10]

It is clear from these studies that ^{13}C n.m.r. spectroscopy will help to clarify the nature of the metal–carbon bond, and may provide a useful method to estimate C–C bond lengths in ligands.

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