Formation of Tetrakis(trifluoromethyl)cyclobutadiene Complexes of Molybdenum and the Existence of High Barriers to Rotation of the Cyclobutadiene Ring

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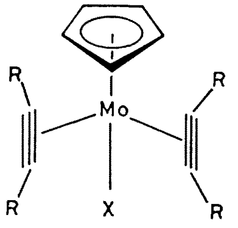
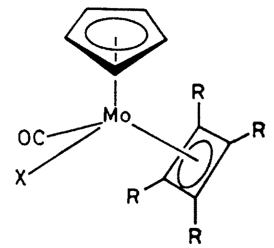
Summary. The syntheses of complexes [Mo(η^5-C_5H_5){η^4-$C_4(CF_3)_4$}(CO)I] and [Mo(η^5-C_5H_5){η^4-$C_4(CF_3)_4$}-S_2CNMe_2] containing a tetrakis(trifluoromethyl)cyclobutadiene ring are described; variable temperature ^{19}F n.m.r. studies reveal the existence of high barriers to rotation of the C_4 ring about the metal–ligand axis in both complexes.



(1) R = CF_3



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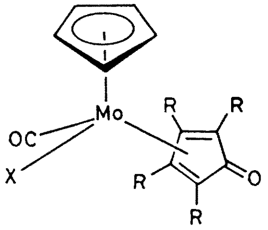


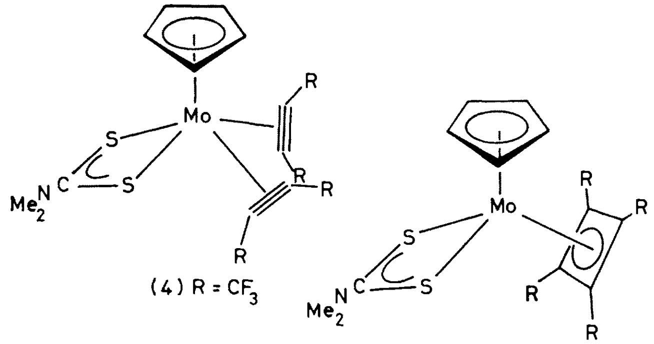
(3) R = CF_3

REACTIONS between acetylenes and metal carbonyls frequently lead to complexes containing cyclobutadiene ligands formed by metal-induced cyclodimerisation of the alkyne.[1] In contrast, electrophilic acetylenes such as hexafluorobut-2-yne (hfb) have not previously been observed to form cyclobutadienes; instead metallocyclopentadiene, benzene, or cyclopentadienone derivatives are formed preferentially.[2] We now report that the reaction of [Mo(η^5-C_5H_5)I$(CO)_3$] with hfb in hexane at 100 °C leads initially to the known[3] bishexafluorobut-2-yne complex (**1**) (X = I) which reacts further in the presence of carbon monoxide to give the first known tetrakis(trifluoromethyl)-cyclobutadiene derivative (**2**) (X = I) and a cyclopentadienone complex [Mo(η^5-C_5H_5)X(CO){$C_4(CF_3)_4CO$}] (X = I), (**3**). In contrast [Mo(η^5-C_5H_5)X$(CO)_3$] (X = Cl[4] or Br) and hfb give (**1**) followed by (**3**) only.

The assignment of structure (**2**) is based on satisfactory elemental analyses and spectroscopic evidence: i.r. (CCl_4) ν(CO) 2067s, ν(CF) 1230s, 1206vs, 1173vs, and 1150w cm^{-1}; n.m.r., ^{1}H ($CDCl_3$) δ 5·80, ^{19}F [$(CD_3)_2CO$, −60 °C, CCl_3F = 0·0 p.p.m.], −50·25, septet, J_{FF} 3·48 Hz (3F), −51·50, septet, J_{FF} 3·15 Hz (3F), −54·77, septet, J_{FF} 3·13 Hz (3F), and −56·74 p.p.m., septet, J_{FF} 3·41 Hz (3F); mass spectra *m/e* 640 (M^+) and ions M^+ −CO and M^+ −(CO + F). The fact that each CF_3 exhibits identical coupling with two other CF_3 groups in the ^{19}F n.m.r. spectrum argues convincingly for the existence of a high-symmetry C_4 ring

Complexes (**1**) (X = Cl) and (**2**) react with NaS_2CNMe_2 at 20 °C in tetrahydrofuran to give isomeric complexes (**4**) and (**5**) respectively. It was subsequently found that the thermal isomerisation of (**4**) into (**5**) proceeds readily at 100 °C in hexane.

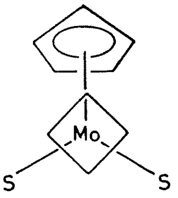
There has been much discussion recently concerning the role of transition metals in promoting symmetry-forbidden reactions. The fact that concerted suprafacial $({}_{\pi}2_{s} + {}_{\pi}2_{s}]$ cyclodimerisation of two acetylenes remains symmetry-forbidden, even if metals intervene in the process, has been cited as an explanation for the failure to observe such reactions.[5] However cyclisations (**1**) → (**2**) and (**4**) → (**5**) clearly demonstrate that pathways exist for such transformations and could indicate that previously proposed stepwise mechanisms involving metallocyclopentadienes,[1,5] may also involve discrete bisacetylene intermediates. The observation that (**1**) (X = Cl, Br) does not undergo a similar transformation to (**2**) [the symmetry-allowed cyclisation to the cyclopentadienone complex (**3**) occurs exclusively] illustrates that a subtle balance of factors influences the availability of such pathways.



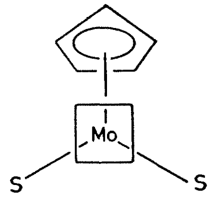
(**4**) R = CF_3

(**5**) R = CF_3

By analogy with the cyclobutadiene complex $[V(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4Ph_4)(CO)_2]$,[6] (**2**), (**4**), and (**5**) can be assigned 'piano-stool' structures. Four CF_3 resonances in the ^{19}F n.m.r. spectrum of (**4**) at 20 °C indicate the absence of a plane of symmetry whereas the three septets in the ^{19}F n.m.r. spectrum of (**5**) (integrated ratio 1:2:1) at −60 °C indicate that the cyclobutadiene ring preferentially adopts conformation (**5a**) rather than (**5b**). *X*-Ray diffraction studies have revealed such an orientation in $[V(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4Ph_4)(CO)_2]$.[6] As the temperature is raised, the three peaks broaden and coalesce to a singlet above 70 °C while the comparable coalescence of the four peaks in the spectrum of (**2**) is observed above 25 °C. This suggests the onset of cyclobutadiene rotation about the metal–ligand axis. The high coalescence temperatures indicate substantial barriers to rotation in marked contrast with complexes containing C_5, C_6, C_7, and C_8 ring systems which invariably have very low barriers.[7] Although steric factors may contribute, the origin of the unexpectedly high rotational barriers in (**2**) and (**5**) may reside in preferential bonding interactions between the cyclobutadiene π-system and the metal fragment[8] which qualitatively appear to be greater in (**5a**) than in (**5b**). A similar explanation accounts for the high barriers to rotation found in isostructural olefin, acetylene, and allyl complexes.[8]



(**5a**)



(**5b**)

Finally it is noted that the sequence of reactions $[Mo(\eta^5\text{-}C_5H_5)I(CO)_3]$ → (**1**) → (**2**) + (**3**) can, by analogy, clarify the mechanistic role of bisacetylene complexes in reactions of acetylenes with $[M(\eta^5\text{-}C_5H_5)X(CO)_3]$ (M = Mo; X = Cl, Br, or I[3,4], M = V, Nb, or Ta; X = CO[9]) which lead to cyclobutadiene and cyclopentadienone analogues of (**2**) and (**3**).

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