

Co-ordinatively Unsaturated Molybdenum and Tungsten Acetylene Complexes. The Mechanisms of Formation of and CO Substitution in $[M(\eta^5-C_5H_5)(SR)(CO)(CF_3C:CCF_3)]$

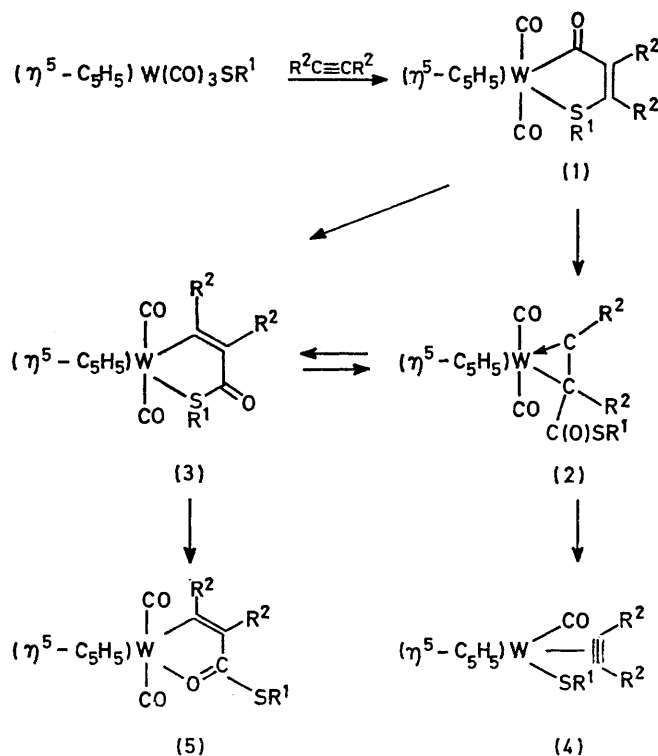
By JACK L. DAVIDSON

(Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS)

Summary Reactions between $[M(\eta^5-C_5H_5)SR^1(CO)_3]$ ($M = W$; $R^1 = Me, Et, \text{ or } Pr^1$) and hexafluorobut-2-yne (hfb) involve initial attack at sulphur and carbonyl ligands to give $[MC(O)C(CF_3):C(CF_3)(SR^1)(\eta^5-C_5H_5)-(CO)_2]$ which undergo stepwise rearrangement to co-ordinatively unsaturated acetylene complexes $[M(\eta^5-C_5H_5)(SR^1)(CO)(hfb)]$; the latter ($M = Mo \text{ or } W, R^1 = C_6F_5$) undergo associative CO substitution reactions with phosphines and phosphites (L) yielding complexes $[M(\eta^5-C_5H_5)(SR^1)(hfb)L]$.

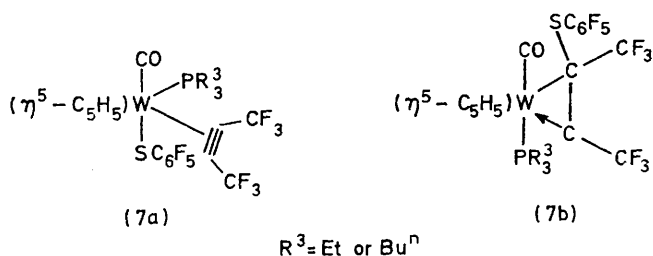
PREVIOUSLY we have reported¹ that hexafluorobut-2-yne (hfb) and dimethyl acetylenecarboxylate (dmad) react with $[W(\eta^5-C_5H_5)(SR^1)(CO)_3]$ ($R^1 = Me, Et, \text{ or } Pr^1$) to give complexes (1) which decompose to (3) *via* novel alkyl-carbene complexes (see Scheme) while with $R^1 = CF_3$ or C_6F_5 co-ordinatively unsaturated acetylene π -complexes (4) are obtained.² We now report the results of further studies which indicate that alkyl-carbene complexes (2) and (7b), respectively, are involved in the formation and CO-substitution reactions of acetylene complexes (4).

Thermal rearrangement of (2; $R^1 = Me \text{ or } Et, R^2 = CF_3$) at 45 °C in diethyl ether ultimately produces (4) and (5) but (3) is produced in the early stages of the reaction. Similarly, (3) reacts to give (4) and (5) but initially (2) is also produced. With the dmad complex (1; $R^1 = Me$) the simplified sequence (1) \rightarrow (3) \rightarrow (5) is observed while hfb and $[W(\eta^5-C_5H_5)SR^1(CO)_3]$ ($R^1 = C_6H_5 \text{ or } 4-MeC_6H_4$) gave (4) as the only isolable species although (2) was present in low concentrations throughout the reactions. Thus the displacement of two CO ligands from $[W(\eta^5-C_5H_5)(SR^1)(CO)_3]$ by hfb to give $[W(\eta^5-C_5H_5)(SR^1)(CO)(hfb)]$ proceeds *via* a unique pathway involving initial reaction of hfb with CO and SR^1 ligands followed by isomerisation to give an alkyl-carbene complex (2) and



SCHEME. $R^2 = CF_3 \text{ or } CO_2Me.$

ultimately by regeneration of SR^1 and hfb ligands. In contrast, the predominant mechanism of CO displacement in mononuclear metal carbonyls involves simple S_N1 or S_N2 processes in which the identity of the incoming ligand is retained throughout the reaction.³



The chemistry of complexes (**4**; $M = \text{Mo or W}$, $R^1 = \text{C}_6\text{F}_5$) has also been investigated and CO substitution by $L[\text{PBU}_3^n, \text{PEt}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2, \text{PPh}_3, \text{or P(OMe)}_3]$ occurs at or below room temperature to give $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{SC}_6\text{F}_5)(\text{hfb})\text{L}]$ (**6**). Since successive substitution of CO by other ligands normally deactivates metal carbonyls towards further CO displacement such reactivity is highly unusual and represents remarkable activation of the molecule by a co-ordinated acetylene. In contrast $[\text{W}(\eta^5\text{-C}_5\text{H}_5)\text{Me}(\text{HC}\equiv\text{CH})\text{CO}]$ and phosphines (L) yield CO insertion products $[\text{W}(\eta^5\text{-C}_5\text{H}_5)\{\text{C}(\text{O})\text{Me}\}(\text{HC}\equiv\text{CH})\text{L}]$.⁴ Reactions involving phosphines apparently proceed according to associative mechanisms since in two cases ($M = \text{W}$, $L = \text{PEt}_3$ or PBU_3^n) orange crystalline intermediates were isolated at low temperatures which analysed as $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{SC}_6\text{F}_5)(\text{CO})(\text{hfb})\text{L}]$ (**7**).

Spectroscopic data *e.g.*, $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{SC}_6\text{F}_5)(\text{CO})(\text{hfb})(\text{PEt}_3)]$, ν_{CO} (Nujol) 1915 cm^{-1} ; ^1H n.m.r. (CDCl_3 , -40°C) τ 4.7 (s, 5H), 7.9 (m, 6H), and 8.9 (m, 9H); ^{19}F n.m.r. [$(\text{CD}_3)_2\text{CO}$, -40°C , $\text{CCl}_3\text{F} = 0$ p.p.m.] 51.25 (apparent t, 3F, J 3.3 Hz) and 52.06 p.p.m. (apparent t, 3F, J 2.7 Hz), are consistent with structures (**7a**) or (**7b**) but, significantly, in contrast with (**4**) and (**6**), no $\nu_{\text{C}=\text{C}}$ mode is present in the i.r. spectrum which argues in favour of the alkyl-carbene complex (**7b**) structurally analogous to (**2**).

Assuming the correctness of the assigned structure, it appears that phosphine co-ordination leads to migration of sulphur on to the acetylene followed by CO expulsion and transfer of SC_6F_5 back to the metal, a sequence of reactions related to the transformations (**1**) \rightarrow (**2**) \rightarrow (**4**). It appears that both CO displacement reactions (**1**) \rightarrow (**4**) and (**4**) \rightarrow (**6**) involve alkyl-carbene intermediates; the recent report⁵ of a structural analogue of (**2**) and (**7b**), $[\text{PtW}(\mu\text{-CC}_6\text{H}_4\text{Me-}p)(\text{CO})_2(\text{PMePh}_2)(\eta^5\text{-C}_5\text{H}_5)]$, containing a platinum-carbene ligand therefore indicates that ligands of this structural type may be more widespread.

I thank the S.R.C. for financial support and Dr. A. Boyd and the University of Edinburgh for the use of n.m.r. facilities.

(Received, 11th April 1979; Com. 212.)

¹ J. L. Davidson, M. Shiralian, K. W. Muir, and L. Manojlovic-Muir, *J.C.S. Chem. Comm.*, 1979, 30.

² P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J.C.S. Dalton*, 1976, 241.

³ J. L. Davidson, 'Inorganic Reaction Mechanisms,' Specialist Periodical Reports, vol. 6, pt. 4, ch. 1, The Chemical Society, London, 1979.

⁴ H. G. Alt, *J. Organometallic Chem.*, 1977, 127, 349.

⁵ T. V. Ashworth, J. A. K. Howard, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1979, 42.