

Preliminary communication

**COORDINATIVELY UNSATURATED MOLYBDENUM AND
 TUNGSTEN ACETYLENE COMPLEXES $[M(\eta^5-C_5H_5)Cl(CF_3C\equiv CCF_3)_2]$:
 REACTIONS WITH CHARGED AND UNCHARGED NUCLEOPHILES**

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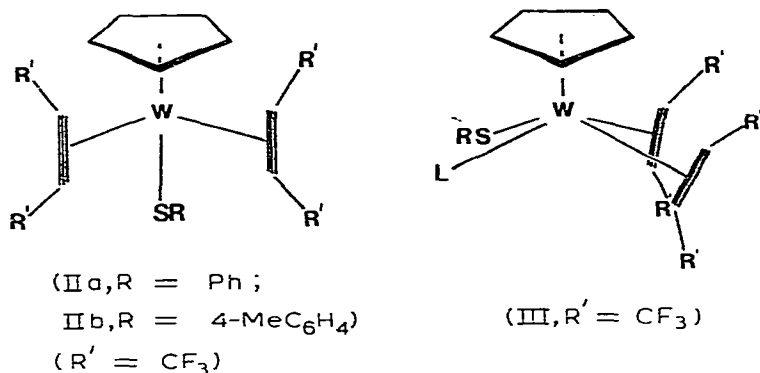
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Summary

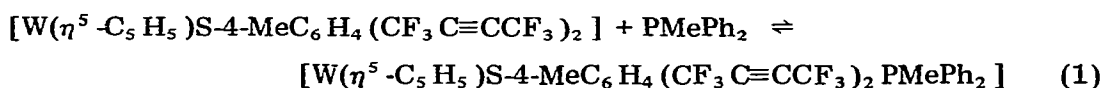
The bis-alkyne complex $[M(\eta^5-C_5H_5)Cl(CF_3C\equiv CCF_3)_2]$ ($M = W$) undergoes metathetical reactions with TISR ($R = Ph, 4-MeC_6H_4, Et, i-Pr$ or $t-Bu$) to give complexes of stoichiometry $[W(\eta^5-C_5H_5)SR(CF_3C\equiv CCF_3)_2]$ which, with the more electron donating groups R , exist as sulphur-bridged dimers. Thallium acetate gives $[M(\eta^5-C_5H_5)MeC(O)O(CF_3C\equiv CCF_3)_2]$ ($M = Mo, W$) with a monodentate acetate ligand while $Na S_2CNR_2$ ($R = Et$) gives $[M(\eta^5-C_5H_5)S_2CNR_2(CF_3C\equiv CCF_3)_2]$ ($M = Mo, W$) containing a bidentate dithiocarbamate ligand. $[W(\eta^5-C_5H_5)S-4-MeC_6H_4(CF_3C\equiv CCF_3)_2]$ gives 1/1 adducts in reactions with uncharged nucleophiles PEt_3, PMe_2Ph and $P(OMe)_3$. Acetylene propeller rotation is observed in several of these derivatives.

Previous studies have established that coordinatively unsaturated bis-acetylene complexes $[M(\eta^5-C_5H_5)X(CF_3C\equiv CCF_3)_2]$ ($M = Mo, W; X = Cl, Br, I$) (a) exhibit fluxional behaviour involving propeller rotation of the alkynes about the metal-alkyne axes [1], (b) react with charged nucleophiles $C_6F_5S^-$ to give fluxional analogues $[M(\eta^5-C_5H_5)SC_6F_5(CF_3C\equiv CCF_3)_2]$ [2], (c) form 1/1 adducts $[M(\eta^5-C_5H_5)X(L)(CF_3C\equiv CCF_3)_2]$ with uncharged nucleophiles $L = PR_3$, which are stereochemically rigid [3]. Complexes $[M(\eta^5-C_5H_5)X(CF_3C\equiv CCF_3)_2]$ ($I, X = Cl$) are the acetylene analogues of highly reactive intermediates $[M(\eta^5-C_5H_5)X(CO)_2]$ thought to be involved in CO substitution reactions of $[M(\eta^5-C_5H_5)X(CO)_3]$ ($X = Cl$) [4]. Consequently studies of I are of particular interest since a knowledge of their chemical behaviour may enable a greater understanding of the mechanistic details of CO dissociative reactions to be achieved. We now report studies of reactions between $[M(\eta^5-C_5H_5)Cl(CF_3C\equiv CCF_3)_2]$ and nucleophiles which illustrate that the nature of ligand X in $[M(\eta^5-C_5H_5)X(CF_3C\equiv CCF_3)_2]$ has a significant effect on achievement of coordinative saturation by the complex.

Reactions of TISR ($R = \text{Ph}, 4\text{-MeC}_6\text{H}_4$) with $[\text{M}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2]$, ($M = \text{W}$) in THF or diethyl ether at 20°C gives monomeric coordinatively unsaturated derivatives (IIa, IIb) which exhibit a single CF_3 resonance in their ^{19}F NMR spectrum down to -90°C . Thus the acetylene propeller rotation indicated by this behaviour, which only becomes significant above -22°C in the parent chloride [5], must occur with substantially lower barrier heights in the mercapto derivatives.

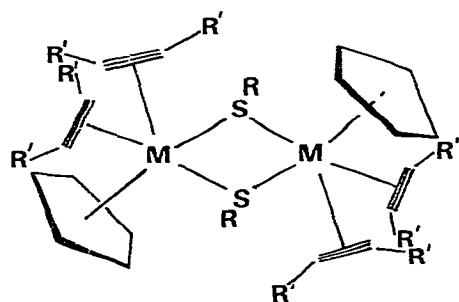


Addition of phosphines $L = \text{PEt}_3, \text{PMe}_2\text{Ph}$ or $\text{P}(\text{OMe})_3$ to IIb gives coordinatively saturated 1/1 adducts (III) analogous to the halide complex $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2\text{PPh}_3]$ reported previously [3]. These derivatives exhibit four distinct CF_3 signals in the ^{19}F NMR spectrum at 20°C and appear to be stereochemically rigid. In contrast $\text{P}(\text{OPh})_3, \text{PBz}_3$ and PPhCy_2 do not react with IIb while with PMePh_2 a yellow crystalline 1/1 adduct is obtained at -20°C . However this dissociates in solution according to ^1H and ^{19}F NMR studies which indicate that the temperature dependent equilibrium 1 is set up. Thus both steric and electronic effects appear to exert



a significant effect on such reactions.

Complexes obtained from the reactions of I ($M = \text{W}$) with TISR ($R = i\text{-Pr}, t\text{-Bu}$) exhibit spectral features similar to those of III i.e. unlike II they are non-fluxional and this can be explained in terms of structure IV. The sulphur



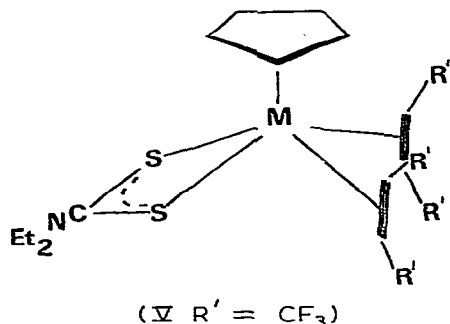
(IVa, $R = i\text{-Pr}; R' = \text{CF}_3$)
 IVb, $R = t\text{-Bu}; R' = \text{CF}_3$)

atoms are presumably sufficiently basic as to enable coordination to a second metal whereas with $R = C_6F_5$, Ph or 4-MeC₆H₄, this is not the case.

Dimerisation via acetylene bridges as observed with $[Nb_2(\eta^5-C_5H_5)_2(CO)_4-(PhC\equiv CPh)_2]$ [6] and $[Mo_2(\eta^5-C_5H_5)_2Cl_2(CF_3C\equiv CCF_3)_2]$ [1] seems less probable since the IR spectra of IVa and IVb exhibit $\nu(C\equiv C)$ modes at 1869 and 1858 cm^{-1} , respectively, which compare with 1863 cm^{-1} in III ($L = PET_3$) but contrast with 1550 and 1521 cm^{-1} in $[Mo_2(\eta^5-C_5H_5)_2Cl_2-(CF_3C\equiv CCF_3)_2]$ [1]. Intermediate behaviour is observed with $[W(\eta^5-C_5H_5)SEt(CF_3C\equiv CCF_3)_2]_n$ which exists in both forms at $-120^\circ C$ according to ^{19}F NMR spectral evidence. Two equal intensity peaks -55.2 and -56.2 ppm are ascribed to a stereochemically rigid structure (II), while three multiplets -53.99 (3F), -56.96 (6F), and -57.90 ppm (3F) are characteristic of the dimeric form IV. The peaks due to II coalesce to a singlet above ca. $-75^\circ C$ as propeller rotation commences while the ultimate coalescence of the resulting four signals to a singlet at -57.35 ppm above $+60^\circ C$ can be explained in terms of either rapid exchange between II and IV or the existence of the monomeric form II only at such temperatures. A similar situation has been established with the but-2-yne complex $[Mo(\eta^5-C_5H_5)SMe(MeC\equiv CMe)_2]$ [7] and is related to equilibrium 1 described earlier.

The effect of the mercapto substituent on the dimerisation tendency of monomer II follows a similar trend to that found with $[M(\eta^5-C_5H_5)SR(CO)_3]$ [8]. With $M = Mo, W, R = C_6F_5$ the dimerisation to $[M_2(\eta^5-C_5H_5)_2(SC_6F_5)_2(CO)_4]$ cannot be induced whereas the instability of $[Mo(\eta^5-C_5H_5)SMe(CO)_3]$ is such that only the dimer is isolable. This is not unexpected since $[M(\eta^5-C_5H_5)SR(CO)_2]$, the carbonyl analogue of II, is a possible intermediate in such dimerisation reactions [4].

Reactions of $[M(\eta^5-C_5H_5)Cl(CF_3C\equiv CCF_3)_2]$ ($M = Mo, W$) with salts of potentially bidentate ligands $LL = acetate, MeCO_2^-$ or dithiocarbamate $R_2NCS_2^-$ ($R = Et$), give complexes $[M(\eta^5-C_5H_5)(CF_3C\equiv CCF_3)_2LL]$ which exhibit comparable trends. Thus the acetate derivatives exhibit two CF_3 peaks at $-90^\circ C$ in the ^{19}F NMR spectrum which coalesce to a singlet above $-40^\circ C$, $M = Mo$; and $0^\circ C$, $M = W$, suggesting that the acetate group is monodentate and that the acetylenes rotate freely. Barriers to rotation are ΔG^\ddagger 50 $kJ mol^{-1}$, $M = Mo$; ΔG^\ddagger 56 $kJ mol^{-1}$, $M = W$. In contrast the dithiocarbamate ligand appears to form stereochemically rigid chelate complexes (V) since four CF_3 resonances (cf. III) are observed in all cases at $20^\circ C$.



These results indicate that the basicity of donor groups of ligand X in $[M(\eta^5-C_5H_5)X(CF_3C\equiv CCF_3)_2]$ play a significant role in determining whether or not the complexes achieve coordinative saturation, a feature we are at present investigating in more detail. It is therefore apparent that, due to its low σ -donor ability, CO will not form stable complexes $[M(\eta^5-C_5H_5)XCO-(RC\equiv CR)_2]$ ($M = Mo, W, X = Cl, Br, I$). Thus the isolation of coordinatively unsaturated acetylene complexes $[M(\eta^5-C_5H_5)X(RC\equiv CR)_2]$ rather than the former from the reactions of $[M(\eta^5-C_5H_5)X(CO)_3]$ with acetylenes [1] is explained.

Acknowledgement

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