# Reactions of 16-Electron Bis-acetylene Molybdenum and Tungsten Complexes with Isocyanides, Dienes, and Trispyrazolylborate Anion; Crystal and Molecular Structure of $[Mo\{(C_3H_3N_2)_2C_3(CF_3)_3CH(CF_3)\}(\eta^5\text{-}C_5H_5)]$

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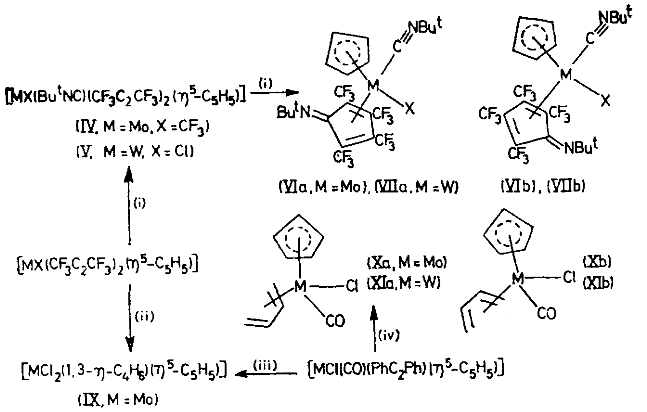
*Summary* Complexes $[MX(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ react with (a) isocyanides to form *N*-alkyltetrakis(trifluoromethyl)cyclopentadienimine compounds (M = Mo, X = $CF_3$; M = W, X = Cl), (b) buta-1,3-diene to give a 17-electron complex (M = Mo, X = Cl), and (c) potassium trispyrazolylborate to give an unusual electronegatively substituted $\eta^3$-allylic system, (M = Mo, X = Cl), the identity of which has been established by a single crystal *X*-ray diffraction study.

We have previously reported[1] the synthesis and structural characterisation of the 16-electron species $[MX(RC_2R)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, W). We now describe initial studies of reactions of these unusual complexes.



Scheme. (i) Bu$^t$NC in $Et_2O$, 1:1 molar ratio of reactants; (ii) $CH_2:CHCH:CH_2$ in hexane; (iii) $CH_2:CHCH:CH_2$ in $CH_2Cl_2$; (iv) $CH_2:CHCH:CH_2$ in THF.

Treatment of $[MoCl(PhC_2Ph)_2(\eta^5\text{-}C_5H_5)]$ with an excess of Bu$^t$NC in $CH_2Cl_2$ at room temperature affords the monoacetylene cationic complex $[Mo(PhC_2Ph)(Bu^tNC)_3(\eta^5\text{-}C_5H_5)]^+$ (I) isolated as its hexafluorophosphate salt. A similar reaction between the mixed acetylene complexes $[MCl(PhC_2Ph)(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) and Bu$^t$NC in $Et_2O$ led to displacement of diphenylacetylene and formation of the complexes $[M(CF_3C_2CF_3)(Bu^tNC)_3(\eta^5\text{-}C_5H_5)]Cl$ (II; M = Mo) and (III; M = W). Previously[2] the cations $[Mo(RNC)_4(\eta^5\text{-}C_5H_5)]^+$ have been obtained by reaction of $[MoX(CO)_3(\eta^5\text{-}C_5H_5)]$ (X = Cl, Br, I) with isocyanide under vigorous conditions. In contrast, treatment ($Et_2O$, room temperature) of $[MX(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, X = $CF_3$; M = W, X = Cl) with Bu$^t$NC (1:1) gave the 18-electron species (IV) and (V) (see Scheme). With a 2:1 molar ratio of reactants the reaction proceeded *via* (IV) and (V) to give respectively isomeric mixtures of the complexes (VI; M = Mo, X = $CF_3$) [$\nu_{NC}$ 2180s, 2170s, and 1685s $cm^{-1}$] and (VII; M = W, X = Cl) [$\nu_{NC}$ 2198s and 1690s $cm^{-1}$], which are assigned the two illustrated structures containing a co-ordinated *N*-t-butyltetrakis(trifluoromethyl)cyclopentadienimine. In an analogous manner, $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ with CO affords the related cyclopentadienone complex $[MoCl(CO)\{(CF_3)_4C_4CO\}(\eta^5\text{-}C_5H_5)]$ (VIII) [$\nu_{CO}$ 2000vs and 1606s $cm^{-1}$]. The complexes (VI), (VII), and VIII) have temperature-dependent $^1H$ and $^{19}F$ n.m.r. spectra consistent with the presence in solution of isomeric species, *e.g.*, (VIa) and (VIb).

Formation of (VI) and (VII) is important in that cyclisation of two acetylene molecules and one isocyanide molecule within the co-ordination sphere is demonstrated, thus providing an understanding of the mode of formation of organic nitrogen compounds in the Ni-, Pd-, and Co-catalysed[3-5] reaction of acetylenes and Bu$^t$NC.

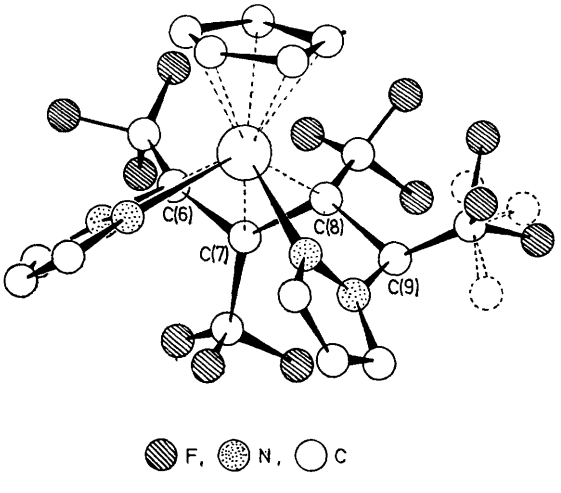


Figure. Molecular structure of (XII).

The 16-electron acetylene complexes also react with 1,3-dienes. Treatment (70 °C) of $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ with buta-1,3-diene in hexane, or of $[MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ with buta-1,3-diene in $CH_2Cl_2$, afforded the paramagnetic 17-electron species (IX), which was characterised by elemental analysis, i.r., and mass spectroscopy. In tetrahydrofuran (70 °C), buta-1,3-diene and $[MCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (M = Mo, W) give respectively the 18-electron complexes (X; M = Mo) [$\nu_{CO}$ 1972 $cm^{-1}$] and (XI; M = W) [$\nu_{CO}$ 1952 $cm^{-1}$]. The $^1H$ n.m.r. spectrum in each case shows a single $\eta^5\text{-}C_5H_5$ resonance, and resonances characteristic of 1—4-$\eta^4$ bonded buta-1,3-diene consistent with either structure (a) or (b). Complexes of this type have not been previously reported and cannot be obtained by reaction of buta-1,3-diene with $[MCl(CO)_3(\eta^5\text{-}C_5H_5)]$. This serves to emphasise the lability of the 16-electron species and their potential value as synthetic reagents. Whereas $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ reacts with $TlC_5H_5$ to give a complex in which the $C_5$ ring is linked to one acetylene and the other acetylene remains $\pi$-bonded, the corresponding reaction with potassium trispyrazolylborate afforded an orange-red crystalline complex (XII), the structural identity of which could not be established by n.m.r. spectroscopy. However, a single crystal *X*-ray diffraction study established the unusual structure shown in the Figure. *Crystal data:* monoclinic, space group $P2_1/n$, $a = 8{\cdot}242(4)$, $b = 17{\cdot}537(9)$, $c = 14{\cdot}651(7)$ Å, $\beta = 97{\cdot}62(5)°$; $Z = 4$; $R$ 0·065 for 2512 reflections [Syntex $P2_1$ four-circle diffractometer, Mo-$K_\alpha$ *X*-radiation, $\lambda = 0{\cdot}71069$ Å].

The molybdenum is essentially seven co-ordinate, showing a $\eta^3$-allylic linkage to three of the four carbon atoms of two condensed hexafluorobut-2-yne molecules. The two pyrazole rings are each $\sigma$-bonded to the Mo atom *via* one of the nitrogen atoms [mean Mo–N 2·17(1) Å], the $\eta^5$-$C_5H_5$ ring occupying the remaining three co-ordination sites. The fourth carbon atom, C(9), of the extended ring system, which carries a hydrogen atom, has a disordered $CF_3$ group. Important parameters for the electronegatively substituted $\eta^3$-allylic system are C(6)–C(7) 1·50(1), C(7)–C(8) 1·48(1), Mo–C(6) 2·14(1), Mo–C(7) 2·14(1), and Mo–C(8) 2·15(1) Å, indicating a symmetrically bonded complex. Although fluorine-substituted Mn[6] and Co[7] $\eta^3$-allyl complexes have been previously observed, formation of (XII) is unusual and must involve fragmentation of the trispyrazolylborate ligand.

A preliminary study of the reaction of $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ with bicyclo[2,2,1]heptadiene indicates that the product $[MoCl\{(C_7H_8)(CF_3)_4C_4\}(\eta^5\text{-}C_5H_5)]$ has a similar $\eta^3$-allylic system to that found in (XII).

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