

The Mechanism of Metal-promoted Alkyne Cyclo-oligomerisation with Isocyanides leading to Cyclopentadiene Derivatives. The Crystal and Molecular Structure of $[\text{WSPri}(\text{CNBu}^t)\{\eta^2\text{-C}_4(\text{CF}_3)_4\text{CNBu}^t\}\{\eta^5\text{-C}_5\text{H}_5\}]$ containing an η^2 -Tetrakis-(trifluoromethyl)cyclopentadienimine Ligand

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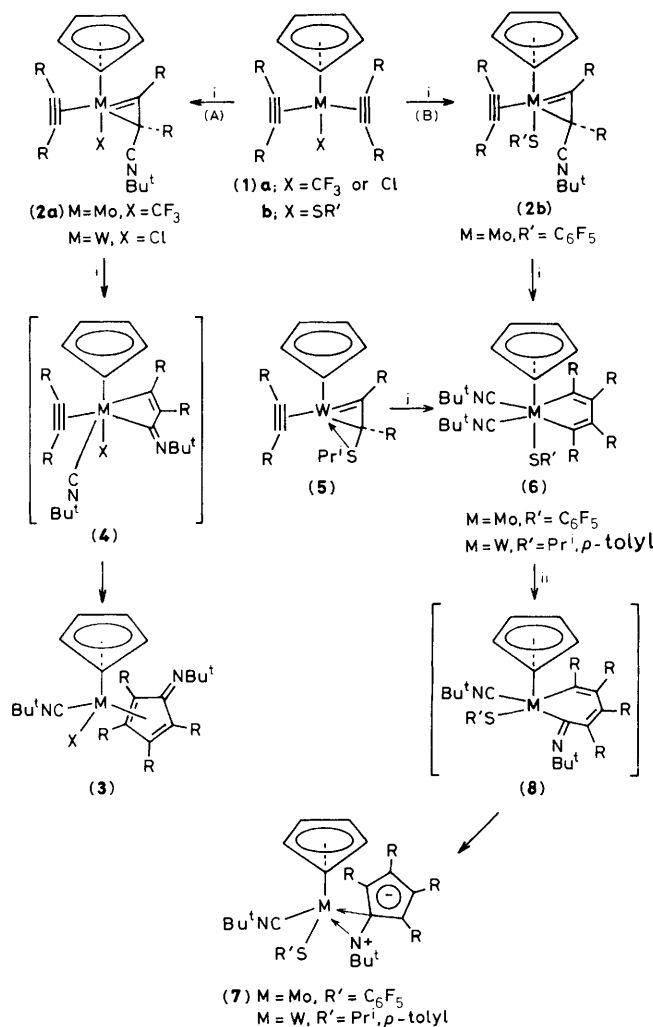
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Reaction of *t*-butyl isocyanide with the two co-ordinated alkynes in $[\text{MSR}'(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, $\text{R}' = \text{C}_6\text{F}_5$; $\text{M} = \text{W}$, $\text{R}' = p\text{-tolyl}$) has been shown to involve initial attack at the alkyne followed by transfer of CNBu^t to the metal with concomitant oxidative metalocyclisation and subsequent reductive cyclisation to give $[\text{MSR}'(\text{CNBu}^t)\{\eta^2\text{-C}_4(\text{CF}_3)_4\text{CNBu}^t\}\{\eta^5\text{-C}_5\text{H}_5\}]$ shown by X-ray diffraction studies ($\text{M} = \text{W}$, $\text{R}' = \text{Pri}$) to contain a tetrakis(trifluoromethyl)cyclopentadienimine ligand attached only *via* the C-N bond to the metal.

The ability of metals to promote cyclisation reactions of alkynes with other organic species has attracted much attention in the last few years and in many cases intermediate metalocyclopentadienes are involved.¹ Previously we have reported that cyclisation with CNBu^t and possibly CO to give cyclopentadienimine and cyclopentadienone derivatives proceeds *via* η^2 -vinyl complexes $[(\mathbf{1a}) \rightarrow (\mathbf{2a}) \rightarrow (\mathbf{3})$ in Scheme 1] thus suggesting an alternative mechanism involving metalocyclobutene intermediates^{2b,3} ($\mathbf{4}$), *i.e.* path A in Scheme 1. We now provide evidence for a mechanism (path B) involving an η^2 -vinyl \rightarrow metalocyclopentadiene transformation and in addition illustrate a novel η^2 -bonding mode for the final product of cyclisation, a cyclopentadienimine ligand.

Reactions of Bu^tNC with the bis alkyne complexes $[\text{MSR}'(\text{CF}_3\text{C}\equiv\text{CCF}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ ($\mathbf{1b}$) ($\text{M} = \text{Mo}$, $\text{R}' = \text{C}_6\text{F}_5$; $\text{M} = \text{W}$, $\text{R}' = p\text{-tolyl}$) or the isomeric η^2 -vinyl derivative ($\mathbf{5}$) ($\text{M} = \text{W}$, $\text{R}' = \text{Pri}$)⁴ proceed as shown in Scheme 1 (path B) to give ($\mathbf{7}$). In the case of ($\mathbf{1b}$; $\text{M} = \text{Mo}$, $\text{R}' = \text{C}_6\text{F}_5$) the full sequence ($\mathbf{1b}$) \rightarrow ($\mathbf{2b}$) \rightarrow ($\mathbf{6}$) \rightarrow ($\mathbf{7}$) is observed illustrating that initial formation of the η^2 -vinyl ($\mathbf{2b}$) is followed by transfer of CNBu^t to the metal. Subsequent metalocyclisation gives isolable intermediates ($\mathbf{6}$) ($\text{M} = \text{Mo}$, $\text{R}' = \text{C}_6\text{F}_5$; $\text{M} = \text{W}$, $\text{R}' = \text{Pri}$ or *p*-tolyl) thus indicating that metalocyclobutenes ($\mathbf{4}$)^{2b,3} are not the direct precursors to the final cyclic products. Instead the final cyclisation ($\mathbf{6}$) \rightarrow ($\mathbf{7}$) presumably results from the alternative insertion of CNBu^t into an M-C bond of the metalocycle giving the undetected interme-



Scheme 1. $R = CF_3$. i, $CNBU^t$ [2 equiv. for (5)]- Et_2O , $20^\circ C$; ii, hexane, $70^\circ C$

diene (8) followed by reductive cyclisation to the cyclopentadienimine derivative as proposed previously.^{2a} The structure of the key intermediate (6) is based on spectroscopic data: e.g. $M = Mo, R' = C_6F_5$, i.r. (CH_2Cl_2) $\nu(C\equiv N)$ 2186m and 2166m cm^{-1} ; 1H n.m.r., ($[^2H_6]$ acetone) δ 5.17 (s, 5H, C_5H_5) and 1.49 (s, 18H, $CNBu^t$); ^{19}F n.m.r., ($[^2H_6]$ acetone) δ -49.65 (m, 6F, CF_3), -55.46 (m, 6F, CF_3), -126.60 (m, 2F, C_6F_5), -159.50 (m, 1F, C_6F_5), and -164.60 p.p.m. (m, 2F, C_6F_5). In particular the presence of a plane of symmetry is revealed by the presence of two CF_3 peaks in the ^{19}F n.m.r. spectra similar to those of the dinuclear metallocycle $[(\eta^5-C_5H_5)(CO)_2Mo-C(CF_3)=C(CF_3)-C(CF_3)=C(CF_3)Co(CO)_2]$ previously characterised by X-ray diffraction studies.⁵

These reactions provide, to our knowledge, the first fully characterised sequence of transformations which clearly identify the mechanism by which two co-ordinated alkynes and a third ligand cyclise within the co-ordination sphere of a metal. Analogies exist with cyclisations involving cobalt metallocycles^{1,3,6} although bis alkyne precursors have only been inferred but not isolated in such reactions. In contrast cyclisation of co-ordinated alkene and alkyne ligands has been reported to give metalcyclopentenes in rhodium based systems⁷ but in none of these cases was initial attack at the alkyne observed giving η^2 -vinyl intermediates.

The final product of cyclisation in the molybdenum and tungsten based system described previously² was shown by

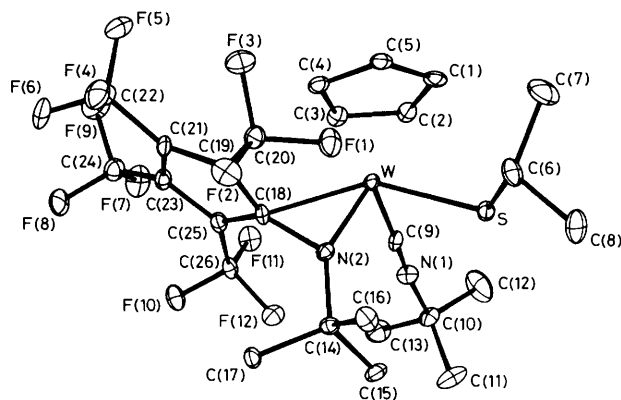
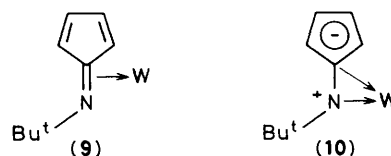


Figure 1. A perspective view of the $[W(SPr^i)(Bu^tNC)-\{(CF_3)_4C_5NBu^t\}(\eta^5-C_5H_5)]$ (7; $M = W, R' = Pr^i$) molecule showing the atom numbering scheme. Hydrogen atoms are omitted. Selected bond lengths are: $W-S$ 2.374(3), $W-C(1)-C(5)$ 2.25(1)-2.51(1), $W-C(9)$ 2.017(9), $C(18)-C(19)$ 1.426(12), $C(19)-C(21)$ 1.385(14), $C(21)-C(23)$ 1.407(14), $C(23)-C(25)$ 1.407(14), and $C(18)-C(25)$ 1.461(13) Å.



X-ray diffraction studies to have structure (3) containing a conventionally bonded η^4 -diene ligand when $X = CF_3$, $M = Mo$.^{2a} However the absence of a $\nu(C=N)$ band near 1700 cm^{-1} in the i.r. spectrum of the thiolato derivatives (7) and the presence of only one isomeric form in solution [(3) exhibits two forms] prompted X-ray diffraction studies of $[WSPri^i(CNBu^t)\{C_4(CF_3)_4CNBu^t\}(\eta^5-C_5H_5)]$ (7; $M = W, R' = Pr^i$). These established the existence of an alternative isomeric form shown in Figure 1† in which the W atom is bonded in a fairly conventional manner to Bu^tNC , SPr^i , and $\eta^5-C_5H_5^-$ ligands, its co-ordination being completed by a cyclopentadienimine derived by condensation of Bu^tNC and two $CF_3C\equiv CCF_3$ molecules. However the last ligand is unexpectedly attached to the metal in an η^2 -fashion through its exocyclic C-N bond, the $W-N(2)$ and $W-C(18)$ distances of 1.90(7) and 2.336(9) Å respectively being notably asymmetric.

Moreover, a careful inspection of the geometry of the W complex indicates that it is not consistent with conventional Chatt-Dewar π -donation from a $C=N$ bond [structure (9)] (e.g. ref. 8). Instead we consider that the zwitterionic cyclopentadienyl structure (10) is more appropriate. It is

† **Crystal Data:** $C_{26}H_{30}F_{12}N_2SW$, $M = 814.4$, monoclinic, $a = 13.082(5)$, $b = 13.988(5)$, $c = 17.554(8)$ Å, $\beta = 110.64(3)^\circ$, $U = 3006$ Å³, $F(000) = 1592$, $D_c = 1.800$ g cm^{-3} , $Z = 4$, space group $P2_1/c$, $Mo-K\alpha$ X-rays, $\lambda = 0.71069$ Å, $\mu = 40.8$ cm^{-1} . Using an Enraf-Nonius CAD4F diffractometer and a needle crystal ($0.45 \times 0.20 \times 0.10$ mm) 6721 intensities ($2 \leq \theta \leq 22^\circ$) were measured. Correction for crystal decomposition and absorption, merging symmetry-equivalent $|F_o|$ (R 0.032 for 2603 duplicates), gave 2929 reflections with $I \geq 2.5\sigma(I)$. The structure was solved by the heavy atom method and refined by large-block least-squares to R (R') 0.039 (0.048) for 379 parameters. Hydrogen atoms were not included. The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should include the full literature citation for this communication.

consistent with (i) the coplanarity of the five-membered C(18)C(19)C(21)C(23)C(25) ring with N(2) to ± 0.04 Å, (ii) the extensive delocalisation of the ring C-C bonds (C-C 1.39–1.46 Å), (iii) the coplanarity of the three bonds radiating from N(2), (iv) the C(14)–N(2)–C(18)–C(19) and –C(25) torsion angles of 85(1) and $-88(1)^\circ$, and (v) the long N(2)–C(18) bond of 1.417(11) Å. Significant overlap between the C(18) and N(2) p-orbitals is precluded by their near orthogonality. Instead there is substantial mixing of the empty p-orbital on N(2) with filled metal d-orbitals. If the W atom accepts lone pairs from N(2) and C(18) as in (10) it formally attains an 18-electron configuration.

Finally we note the ability of the cyclopentadienimine ligand to adopt two different modes of bonding in basically similar molecules (3) and (7). Conceivably this may reflect differences in the π -donor abilities of the auxiliary ligand X, *i.e.* with X = Cl or CF₃ the η^4 -mode is preferred whereas thiolates, X = SR', result in the η^2 -mode of bonding.

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