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Preliminary communication

ISOMERISM AND FLUXIONAL BEHAVIOUR IN η^2-VINYL COMPLEXES RESULTING IN INVERSION OF CONFIGURATION AT AN ASYMMETRIC CARBON ATOM. THE CRYSTAL AND MOLECULAR STRUCTURES OF TWO ISOMERIC FORMS OF $[MoCl\{\eta^2\text{-}C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$

JACK L. DAVIDSON*, WILLIAM F. WILSON,
Department of Chemistry, Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS (Great Britain)
LJUBICA MANOJLOVIĆ-MUIR and KENNETH W. MUIR*
Department of Chemistry, The University, Glasgow G12 8QQ (Great Britain)

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Summary

η^2-Vinyl complexes $[MCl\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (M = Mo, W: L = tertiary phosphine or phosphite or pyridine) have been shown by NMR and X-ray diffraction studies to exist in two distinct isomeric forms which exhibit (a) different orientations of the η^2-vinyl ligand (b) different configurations at the asymmetric carbon atom of the η^2-vinyl ligand: variable temperature NMR studies reveal fluxional behaviour thought to involve reversible inversion of configuration at this carbon atom.

Recently we reported the synthesis and structures of novel η^2-vinyl complexes $[MX\{\eta^2\text{-}C(CF_3)C(CF_3)L\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ formed by addition of nucleophiles L to coordinatively unsaturated hexafluorobut-2-yne complexes $[MX(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (1, X = Cl, M = Mo, W; X = S-*p*-Tol, M = W) [1]. However more detailed studies of a wider range of this type of complex have now revealed the existence of two isomeric forms of the molecule.

Addition of nucleophiles (L) to $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta\text{-}C_5H_5)]$ (1a) (diethyl ether, 20°C) gives η^2-vinyl complexes $[MoCl\{C(CF_3)C(CF_3)L\}\text{-}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ (2) in moderate to high yields. ^{19}F NMR studies indicated the existence of two distinct isomeric forms, a kinetic isomer (I) isolable when L = PEt_3, $P(OMe)_3$, $P(OEt)_3$, or PMe_2Ph, and a thermodynamic

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isomer (II, L = PPh_3, $P(C_6H_{11})_3$, $PMePh_2$, PMe_2Ph, $P(CH_2Ph)_3$, $P(OPh)_3$, pyridine or $CNBu^t$). Heating isomer I in solution (L = PEt_3, 90°C hexane 2 h; L = PMe_2Ph, 40°C, 2h) gave isomer II in good yield (>70%). In order to establish the nature of the isomerism X-ray studies of both isomeric forms of $[MoCl\{C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ were undertaken.

X-Ray analyses of isomers of $[MoCl\{C(CF_3)C(CF_3)(PEt_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ *(2)*

$C_{19}H_{20}ClF_{12}PMo$ (2), formula wt = 638.7. Isomer I: monoclinic, space group $P2_1/n$, a 9.960(1), b 25.003(2), c 9.380(1) Å, β 89.96(1)° (sic), Z = 4. Isomer II: orthorhombic, space group $Pbcn$, a 17.560(3), b 17.645(2), c 15.148(3) Å, Z = 8.

Unit cell dimensions and intensities ($\omega/2\theta$ scans) for both isomers were measured by standard methods on an Enraf—Nonius CAD4F diffractometer. Hydrogen scattering contributions were included in the final calculations but only U_{iso} for H atoms were refined. Full matrix least-squares refinement converged at R = 0.039, R_w = 0.041 for 5325 reflections (isomer I) and R = 0.031, R_w = 0.043 for 2579 reflections (isomer II). F(1)—F(3) of isomer I are disordered*.

The kinetic product (isomer I) results from addition of PEt_3 to a coordinated acetylenic carbon atom in $[MoCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ to form a dipolar η^2-vinyl ligand $C(CF_3)C(CF_3)PEt_3$ of a type now structurally well-characterised [1—3]. In isomer I the metal-coordinated C—C bonds of both η^2-ligands are nearly parallel with the Mo—Cl bond. In $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ (**1b**) both acetylenic C≡C bonds are also nearly parallel with the W—Cl bond [4]. Assuming that the conformation of **1a** is similar to that of its W analogue **1b** it follows that addition of PEt_3 to **1a** involves attack on one of the sterically more accessible pair of acetylenic carbon atoms from the side of the complex opposite to the C_5H_5 ring. The gross features of the metal coordination polyhedron, and in particular the orientation of the attacked acetylene, are little altered by the reaction. However, the MoC(6)C(7) bonding now approximates to that in a metallated cyclopropene ring, with the Mo—C(6) and Mo—C(7) bonds respectively ca. 0.2 Å shorter and longer than the Mo—C(2) or Mo—C(3) bonds.

The addition of PEt_3 to **1a** leads to the creation of two chiral centres, at C(7) and at Mo. Epimerisation of isomer I (kinetic product) into isomer II (thermodynamic product) involves inversion of configuration at C(7) and retention at Mo, or equivalently, retention at C(7) and inversion at Mo. Both isomers are of course racemic: Fig. 1 and quoted torsion angles refer to molecules with the same configuration at Mo. Apart from configurational change the structures of isomers I and II differ mainly by rotation of the dipolar ligand about the Mo—C(6) bond, so that the Cl—Mo—C(6)—C(7) torsion angle in isomer II is some 30° larger than in isomer I. Corresponding bond lengths, and also bond angles (with the exception of those involving C(7)), in the

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*The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.

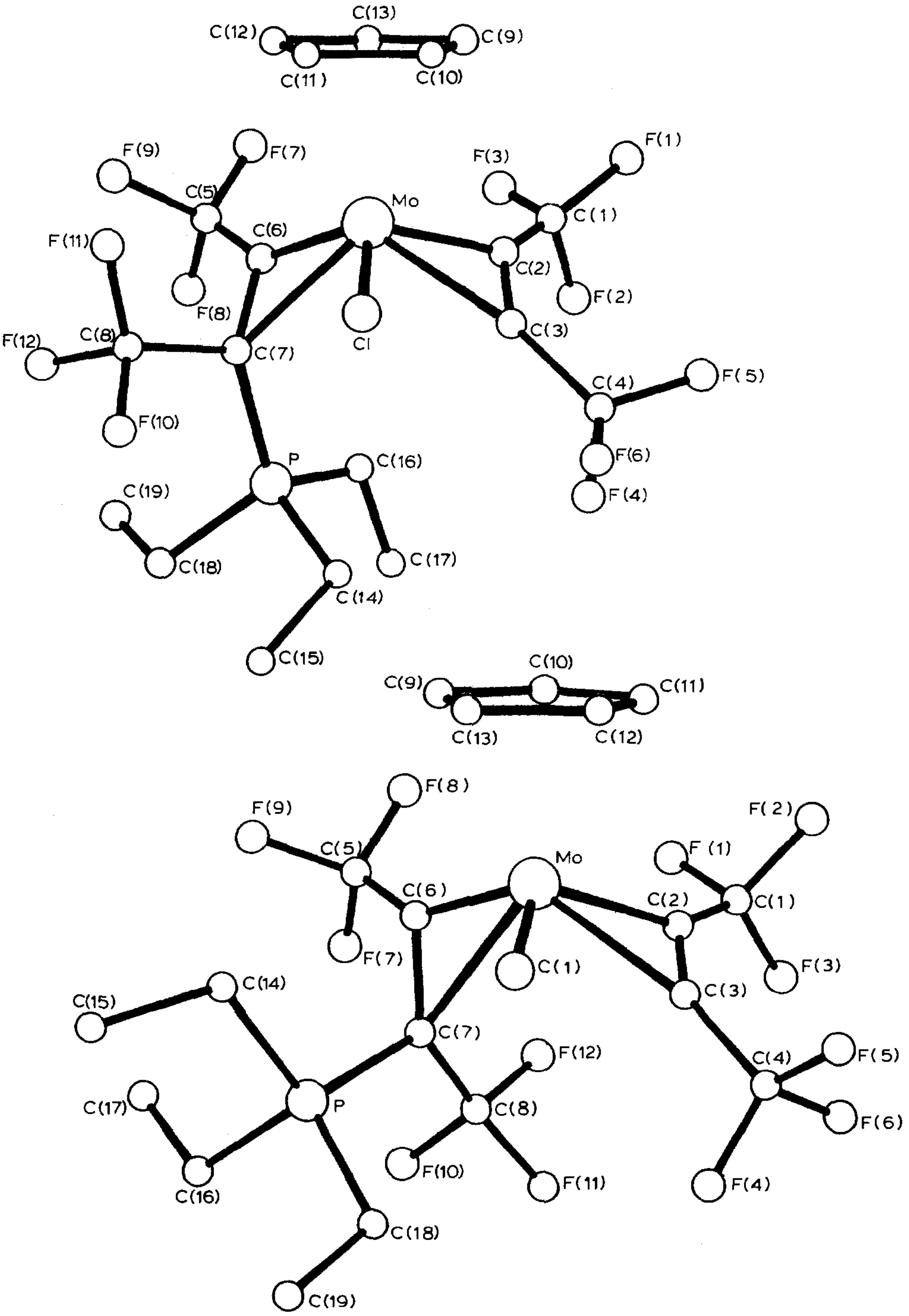
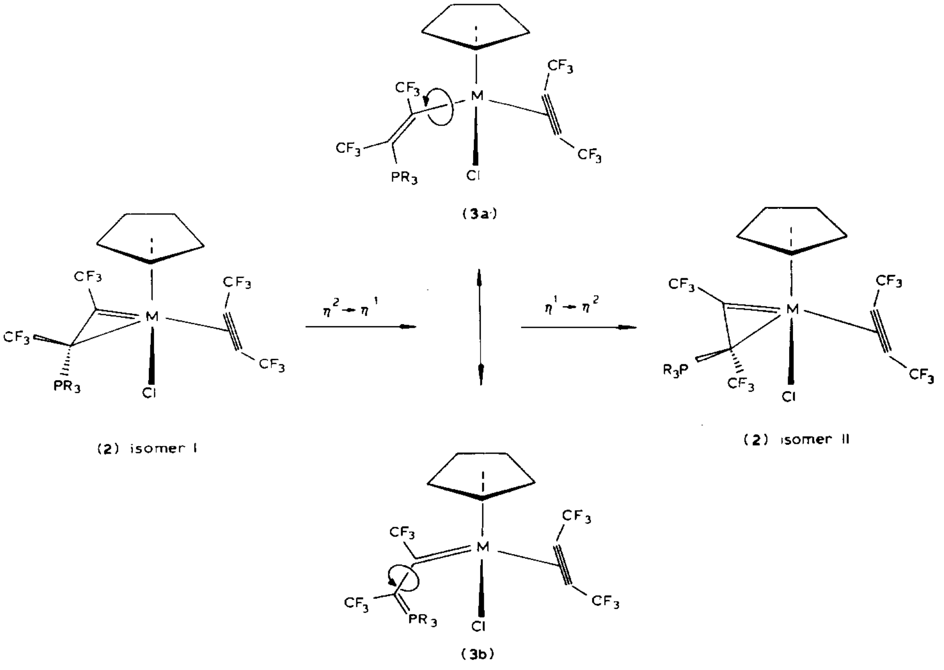


Fig. 1. The molecular structures of the isomeric forms of 2. (a) Isomer I (kinetic product), (b) isomer II (thermodynamic product). Selected distances (Å) and angles (°) in isomers I and II respectively are: Mo—C(2) 2.085(3), 2.080(3), Mo—C(3) 2.149(3), 2.117(5), Mo—C(6) 1.924(3), 1.914(6), Mo—C(7) 2.287(3), 2.322(5), C(6)—C(7) 1.427(5), 1.423(7), Cl—Mo—C(2)—C(3) 13.7(3), 11.8(4), Cl—Mo—C(6)—C(7) −17.4(2), −46.7(4), C(5)—C(6)—C(7)—C(8) −65.6(4), 62.4(8).

two isomers agree well. The greater stability of isomer II must therefore presumably arise from a sterically more favourable arrangement of the ligands about the metal atom. In accord with this the kinetic isomer I can only be isolated with phosphines or phosphites exhibiting low cone angles i.e. with reduced steric requirements.

To account for the isomerisation reaction I → II we propose a mechanism (see Scheme 1) involving reversible formation of an η^1-vinylphosphonium intermediate (**3a**,**3b**) which enables both reorientation and epimerisation to occur via simple rotations. Although epimerisation could conceivably involve configurational change at either chiral centre, Mo or C(7), we favour the latter for the following reasons. Previously [2,3] $\eta^2 \rightarrow \eta^1$ and $\eta^1 \rightarrow \eta^2$ vinyl rearrangements have both been observed under very mild conditions while X-ray diffraction studies have recently established the presence of an η^1-vinyl phosphonium ligand in $[Cr\{\eta^1\text{-}C(OSiMe_3)=CH(PMe_3)\}(CO)_5]$ which undergoes rearrangement (*E* → *Z* isomer) on photolysis [5]. Moreover the M—C(7) distance in both isomers I and II and in other η^2-vinyl complexes [1,2,3] is rather long for an M—C single bond which indicates that the $\eta^2 \rightarrow \eta^1$ vinyl tranformation would not be a high energy process. Significantly intermediate 3 could in principle achieve stabilisation as a result of the alkyne ligand acting as a 4-electron donor to the metal [6] such that the metal maintains the favoured eighteen electron configuration throughout the isomerisation process. The last proposal may have more widespread significance for reactions of acetylene complexes which proceed via dissociative processes.



SCHEME 1

Assuming that an η^1-vinyl intermediate is involved in the formation of isomer II the collapse of the η^1 to the η^2 form could clearly produce both epimers depending on the relative disposition of the CF_3 and PR_3 substituents on the asymmetric carbon atom C(7). Figure 1 illustrates that in this case the preferred isomer is one in which the phosphine is oriented towards the chloro ligand. However variable temperature ^{1}H, ^{19}F and ^{31}P NMR studies of PMe_2Ph and $PMePh_2$ complexes 2 (isomer II) reveal the presence of three isomeric forms at low temperature (–80°C) which interconvert rapidly above ca. –45°C (PMe_2Ph) and ca. +40°C ($PMePh_2$), the ^{19}F NMR resonance associated with one particular CF_3 group being affected significantly by the fluxional process. Although the NMR data do not enable the fluxional process to be defined unequivocally we propose the following explanation. Conceivably the η^2-vinyl ligand can adopt two orientations, the most favoured being that illustrated in Fig. 1 (isomer II) and a sterically less favourable one in which the C(6)—C(7) bond has rotated by ca. 180°. Isomerism of this type has been found in $[Mo\{\eta^2\text{-}C(R^1)C(Ph)R^2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$, ($R^1$ = Me, R^2 = Ph; R^1 = Bu^t. R^2 = H) [7]. Both of these isomers and their epimeric forms could therefore undergo rapid exchange via the η^1-vinyl intermediate 3 (see Scheme 1). Steric factors may dictate that one of these forms is not accessible thus accounting for the presence of only three sets of peaks in the NMR spectra. We note that this mechanism and that in Scheme 1 is analogous to the $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ process which accounts for the exchange of *syn* and *anti* groups in allyl complexes [8].

Previously we have suggested that η^1-vinyl complexes may undergo isomerisation via η^2-vinyl intermediates [1a]. The results reported herein not only provide evidence for the alternative sequence of $\eta^2 \rightarrow \eta^1 \rightarrow \eta^2$ transformations but in addition illustrate that η^2-vinyl complexes have distinct orientational and configurational preferences. Moreover it is conceivable an $\eta^2 \rightarrow \eta^1$ vinyl transformation involving isomer I could lead to a different η^1-vinyl complex to that obtained from isomer II. In this way it may be possible to account for geometric preferences (*E* or *Z*) exhibited by η^1-vinyl complexes isolated from the addition and insertion reactions of alkynes [9] should they be formed via η^2-vinyl intermediates.

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