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Preliminary communication

Metal-promoted insertion and cyclisation reactions of alkynes: the crystal and molecular structures of [Mo{η^4-$C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)SPr^i$}$(PEt_3)$($\eta^5$-$C_5H_5$)] and [Mo{$\eta^1$-$C(CF_3)=C(CF_3)SC_6F_5$}$(CF_3C{\equiv}CCF_3)(O)$($\eta^5$-$C_5H_5$)]

W. Azelee Wan Abu Bakar, Laurence Carlton, Jack L. Davidson *,

Department of Chemistry, Heriot-Watt University, Riccarton, 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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Abstract

Bis-alkyne [$MSR'(CF_3C{\equiv}CCF_3)_2(\eta^5$-$C_5H_5)$] and η^2-vinyl complexes {M(η^3-$C(CF_3)C(CF_3)SR'$}($CF_3C{\equiv}CCF_3$)(η^5-C_5H_5)] (M = Mo, W, R′ = alkyl, aryl or perfluoroaryl) undergo a variety of insertion and oligomerisation reactions which are promoted by coordination of a ligand, e.g. PR_3, O, to the metal centre. This can be rationalised in terms of a switch in the bonding mode of the alkynes from 3- to 2-electron donation to the metal.

Insertion reactions of alkynes into metal–ligand bonds frequently lead to or proceed via η^1-vinyl (alkenyl) complexes [1]. Recently, however, we and others have drawn attention to the role of η^2-vinyl complexes in metal alkyne chemistry [2–4]. For example, we previously reported that phosphines react with bis-alkyne and isomeric η^2-vinyl complexes (**1**) and (**2**) to give η^2-vinyls (**3**) [2a]. We now report reactions of **1**, **2** and **3**, which clarify some aspects of metal-promoted alkyne insertion and oligomerisation reactions which proceed via η^2-vinyl intermediates.

Complex **3** (M = Mo, R′ = C_6F_5, L = $PMePh_2$) isomerises in solution (Et_2O, 20 °C) into **4a**, whereas the analogous complex **4b** was obtained directly (Et_2O, 0 °C) from the reaction of **2a** with triethylphosphine (see Scheme 1). X-ray diffraction studies of **4b** (Fig. 1) revealed that phosphine migration to the metal had occurred, resulting in formation of a $C_4(CF_3)_4SPr^i$ butadienyl ligand bonded to the metal through C(2), C(5), C(7), and S. A fixed C=C double bond is implied by the C(2)–C(3) distance (1.331(5) Å) and the near zero CF_3–C–C–CF_3 torsion angle

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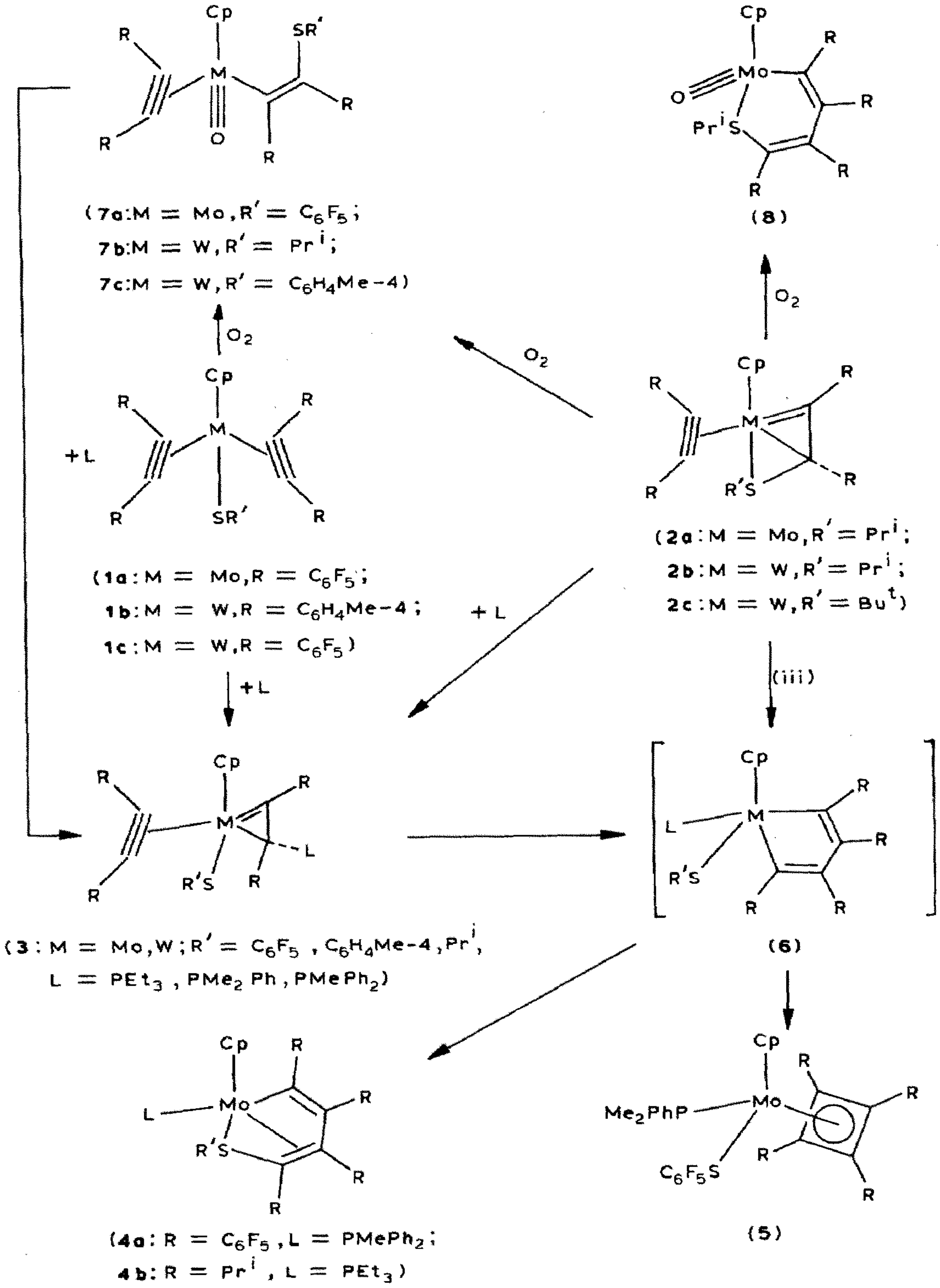


Scheme 1. R = CF_3.

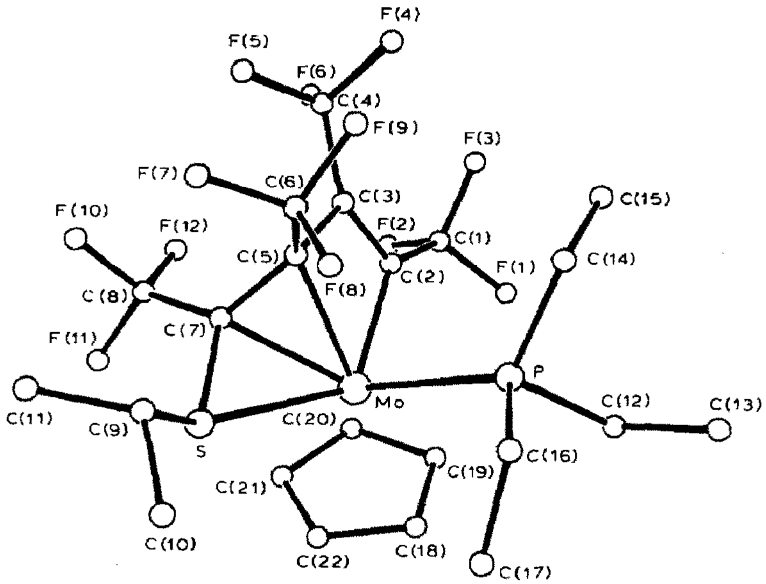


Fig. 1. A view of the $[Mo\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3SPr^i](PEt_3)(\eta^5\text{-}C_5H_5)]$ molecule. Selected distances (Å) are: Mo–P 2.507(1), Mo–S 2.514(1), Mo–C(2) 2.170(4), Mo–C(5) 2.243(3), Mo–C(7) 2.154(3), Mo–C(Cp) 2.270(4)–2.347(4), S–C(7) 1.762(4), S–C(9) 1.850(5), C(2)–C(3) 1.331(5), C(3)–C(5) 1.496(5), C(5)–C(7) 1.456(5).

across C(2)–C(3) (5.7(4)°, df. – 49.4(4) and 102.8(5)° across C(3)–C(5) and C(5)–C(7)]. If the MoC(5)C(7) unit were to be regarded as a metal η-alkene system, **4b** would be a Mo^{II} species, but we consider the Mo^{IV} formulation preferable because the Mo–C(5) and Mo–C(7) distances are at least 0.1 Å shorter than the W–C(π-alkene) distances in $[W\{\eta^4\text{-}C(CF_3)C(CF_3)=C(Me)C(Me)SPr^i\}(\eta^2\text{-}CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ [2b]. The latter also contains a $(CR)_4SPr^i$ ligand but its attachment to the metal through C(carbene), η^2-alkene and σ-C bonds differs from that in **4**.

Thermolysis of **3** (M = Mo, R′ = C_6F_5, L = PMe_2Ph) (refluxing hexane) in contrast gives a cyclobutadiene complex **5** as a result of phosphine transfer to the metal. Spectroscopic data: ^1H NMR ($CDCl_3$) δ 1.83 (d, J(P–H) 9.3 Hz, 3H, Me) 2.0 (d, J(P–H) 9.2 Hz, 3H, Me) 5.29 (d, J(P–H) 1.7 Hz, 5H, C_5H_5), 7.55 (m, 5H, Ph); ^{19}F NMR ($CD_3C_6D_5$, −20 °C), δ −49.19 (bs, 3F), −52.33 (bt, J(F–F) 17.3 Hz, 3F), −53.20 (sept., 3F), −57.07 (b. sept., 3F), −129.9 (m, 2F), −158.1 (t, 1F), −163.46 (m, 2F). Dynamic NMR studies indicate a fixed orientation for the $\eta^4\text{-}C_4(CF_3)_4$ ring at −20 °C such that one CF_3 δ −52.33 couples to the two C_6F_5 *ortho* fluorines. At higher temperatures ring rotation occurs to give one CF_3 resonance at +60 °C, a phenomenon we have observed previously with related complexes [3]. Metal promoted alkyne dimerisation to give cyclobutadienes is thought in most cases to proceed via metallocyclopentadiene intermediates [3], and in the case of **5** a species such as **6** can be evoked. In support of this a related complex R′ = Bu^t, L = $CNBu^t$ has been obtained from the reaction of **2c** with CNBu and fully characterised [4]. More remarkably, a species with similar spectroscopic (NMR) features was detected as an intermediate in the reaction of **2a** with PEt_3 at −50 °C, and this isomerised into **4b** at higher temperatures. Clearly in this case oligomerisation proceeds via phosphine

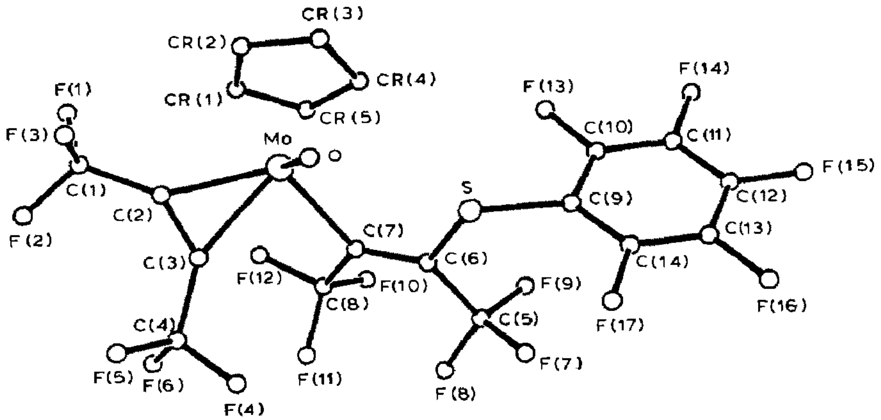


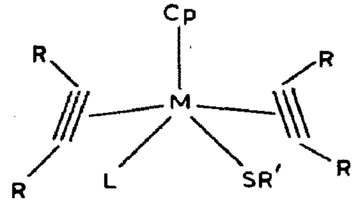
Fig. 2. A view of the $[MoO\{C(CF_3)=C(CF_3)SC_6F_5\}(\eta^2\text{-}CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)]$ molecule. Selected distances (Å) are: Mo–O 1.674(3), Mo–C(2) 2.080(4), Mo–C(3) 2.120(4), Mo–C(7) 2.216(3), Mo–C(Cp) 2.341(4)–2.441(4), C(2)–C(3) 1.270(5), S–C(6) 1.792(3), S–C(9) 1.776(4), C(6)–C(7) 1.337(4).

coordination to the metal followed by metallocyclisation, and ultimately by sulphur migration on to a terminal carbon of the metallocycle in **6**.

Migration of sulphur onto carbon is also observed in reactions of (**1a**, **1b**) and (**2b**) with oxygen (Et_2O, 40 °C) which give oxo-alkenyl complexes 7. X-ray diffraction studies (Fig. 2) reveal that **7a** is formally derived by *cis* insertion of a second $CF_3C\equiv CCF_3$ into the Mo–S bond of $[Mo(SC_6F_5)(O)(CF_3C\equiv CCF_3)(\eta^5\text{-}C_5H_5)$ [5]. As in the latter the 2-electron donor $CF_3C\equiv CCF_3$ is oriented normal to the Mo–O vector (C(3)–C(2)–Mo–O – 90.5(3)°) so that two empty t_{2g} are available for Mo–O triple bond formation while the third filled t_{2g} orbital can function as π-donor to the alkyne.

An oxo complex (**8**) is also obtained on air oxidation of **2a**, but spectroscopic data are consistent with an η^2-butadienyl structure formally derived by *cis* insertion of $CF_3C\equiv CCF_3$ into the Mo–C vinyl bond of a species similar to 7. ^1H NMR ($CDCl_3$) δ 1.32 (overlapping doublets, 6H, Pr^i), 3.60 (m, 1H, Pr^i), 6.18, 6.38, (s, 5H, C_5H_5); ^{19}F NMR ($CDCl_3$) −49.48 (q, $J = 16.3$ Hz), −49.79 (q, J 1b.2 Hz), −54.43 (q, J 16.7 Hz), −55.0 (qq, J 16.4 Hz, J 3.3 Hz), −55.19 (qq, J 13.9 Hz, J 1.7 Hz), −55.47 (qq, J 13.8 Hz, J 3.3 Hz), −58.18 (q, J 13.8 Hz), −58.33 (q, J 13.6 Hz). The spectra reveal the presence of two isomers possibly resulting from inversion at a pyramidal sulphur. The large coupling between two sets of CF_3 groups J ca. 14 and 16 Hz is characteristic of *cis*-$CF_3C=CCF_3$ groups [6] as in the illustrated structure. In contrast with 7 a $\nu(C\equiv C)$ mode is absent from the IR spectrum. We note the structural relationship of **4** and **8** but the ability of O^{2-} to function as a 6-electron donor as in 7 eliminates the requirement for the butadienyl ligand to bond in an η^4-mode as found in the former. Interestingly reactions of **7a**, **7c** (Et_2O, 20 °C) with excess phospine L = PEt_3, PMe_2Ph, or $PMePh_2$ give η^2-vinyls 3 previously obtained from addition of L to alkyne complexes **1** [1,3]. This illustrates remarkably that reduction of the metal, $M^{IV} \rightarrow M^{II}$, reverses the insertion process, so that the thiolate ligand is transferred back to the metal. Conceivably this occurs via phosphine attack on oxygen to give a phosphine oxide, followed by regeneration of the bis-alkyne complex **1**.

In conclusion the reactions in Scheme 1 shows that the kinetic products of nucleophilic attack on bis-alkyne complexes of type **1** are η^2-vinyls **2** and **3**, whereas coordination of ligands e.g. PR_3, O, to the metal invariably results in alkyne insertion or cyclisation. Previously we have noted [4] that activation of 3-electron donor-alkynes in coordinatively unsaturated alkyne complexes **1** may be associated with formation of a coordinatively saturated intermediate such as **9** in which the alkynes function only as two electron donor ligands. The present work not only supports this idea but also illustrates that the nature of the incoming ligand controls the subsequent reaction. In the case L = phosphine metallocyclisation occurs preferentially to give **4** or **5**, whereas with L = O migration of thiolate onto an alkyne is observed in most cases, leading to η^1-alkenyl species **7**. Significantly, removal of oxygen by phosphines reverses the latter reaction.



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* Both structure analyses were carried out on an Enraf–Nonius diffractometer with Mo-K_α radiation, $\lambda = 0.71069$ Å. Empirical absorption corrections were applied for **4b** and **7a**. All H atoms were included in the final calculations and the constraints C–H 0.96 Å and $U(H) = U_{iso}(C)$ applied.

Crystal data: **4b**: $C_{22}H_{27}F_{12}MoPS$, $M = 678.4$, monoclinic, space group $P2_1/n$, a 16.505(4), b 9.386(7), c 18.154(3) Å, β 106.88(2)°, U 2691(2) Å^3, $Z = 4$, D_c 1.674 g cm^{-3}, μ(Mo-K_α) 7.0 cm^{-1}, 334 parameters, $R(R_w) = 0.029(0.035)$ for 3985 intensities $> 3\sigma(I)$ with θ(Mo-K_α) $< 28°$. **7a**: $C_{19}H_5F_{17}MoOs$, $M = 700.2$, triclinic, space group $P\bar{1}$, a 8.561, b 10.627(1), c 12.642(1) Å, α 104.10(1), β 92.45(1), γ 96.77(1)° (reduced cell), U 1104.5(2) Å^3, $Z = 2$, D_c 2.105 g cm^{-3}, μ(Mo-K_α) 8.2 cm^{-1}, 352 parameters, $R(R_w) = 0.035$ (0.044) for 4504 intensities $> 3\sigma(I)$ with θ(Mo-K_α) $< 30°$.

Atomic coordinates are available from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.