

Unprecedented Reactions of Alkynes with η^2 -CS₂ Metal Complexes

Françoise Conan,^a Jacques-E. Guerschais,^a René Mercier,^b Jean Sala-Pala,^a and Loïc Toupet^c

^a U.A. C.N.R.S. 322, Université de Bretagne Occidentale, 29287 Brest-Cedex, France

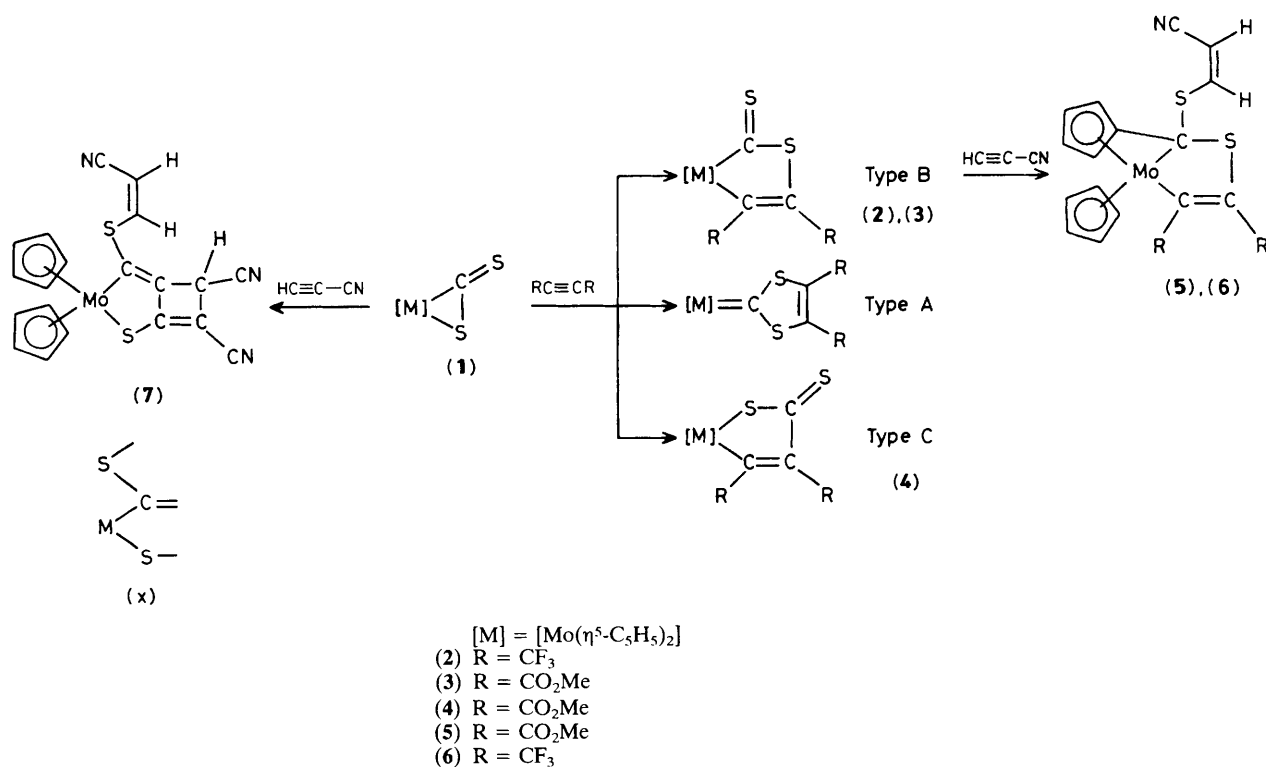
^b U.A. C.N.R.S. 436, Université de Franche-Comté, 25030 Besancon-Cedex, France

^c E.R.A. C.N.R.S. 804, Université de Rennes, 35042 Rennes-Cedex, France

Alkynes react with $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-CS}_2)]$ (**1**) to afford heterocycle derivatives $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo-C(S)-S-C(R)=CR}]$ [**2**] ($\text{R} = \text{CF}_3$); [**3**] ($\text{R} = \text{CO}_2\text{Me}$) and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo-S-C(S)-C(R)=CR}]$ [**4**] ($\text{R} = \text{CO}_2\text{Me}$), and both (**2**) and (**3**) react with $\text{HC}\equiv\text{C-CN}$ to yield $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}\{\eta\text{-C}_5\text{H}_4\text{-C(SCH=CHCN)-S-C(R)=CR}\}]$ [**5**] ($\text{R} = \text{CO}_2\text{Me}$); [**6**] ($\text{R} = \text{CF}_3$), while treatment of (**1**) with $\text{HC}\equiv\text{C-CN}$ gives an unprecedented metallacycle $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{C}_{10}\text{H}_3\text{N}_3\text{S}_2)]$ (**7**), corresponding to the addition of three alkynes to CS_2 ; the structures of (**4**), (**5**), and (**7**) have been established by X-ray crystallography.

The utilization of carbon disulphide in transition metal mediated reactions of complex organic molecules is an important problem. Among the reactions of η^2 -CS₂ metal complexes that could have significant practical applications in organic synthesis is the 1,3-dipolar cycloaddition of electron-deficient alkynes.¹ Depending on the nature of the metal and

of the ancillary ligands, this reaction affords either the 1,3-dithiol-2-ylidenemetal derivative (Scheme 1, type A) or the heterometalloycycle $[\overline{\text{M}}\text{-C(S)-S-C(R)=CR}]$ (type B) $\{[\text{M}] = [\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2]\}$. To our knowledge, compounds with the third type of metalocycle in Scheme 1 (type C) have not been obtained previously from reactions between $\text{M}-(\eta^2\text{-CS}_2)$



Scheme 1. Reactivity of alkynes towards η^2 -CS₂ metal complexes.

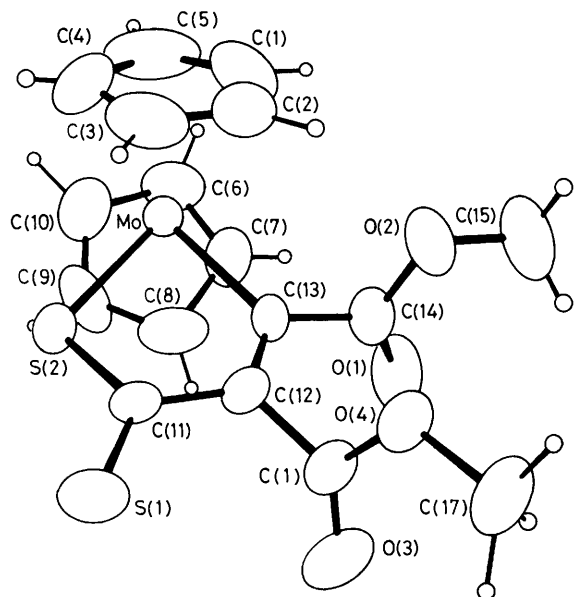


Figure 1. Molecular structure of one of two crystallographically distinct molecules of (4) (the other molecule shows similar features). Selected bond lengths (Å) and angles (°): Mo–C(13) 2.183(2), C(13)–C(12) 1.354(3), C(12)–C(11) 1.460(3), C(11)–S(2) 1.713(2), S(2)–Mo 2.440(1), C(11)–S(1) 1.649(2), S(2)–Mo–C(13) 77.3(2).

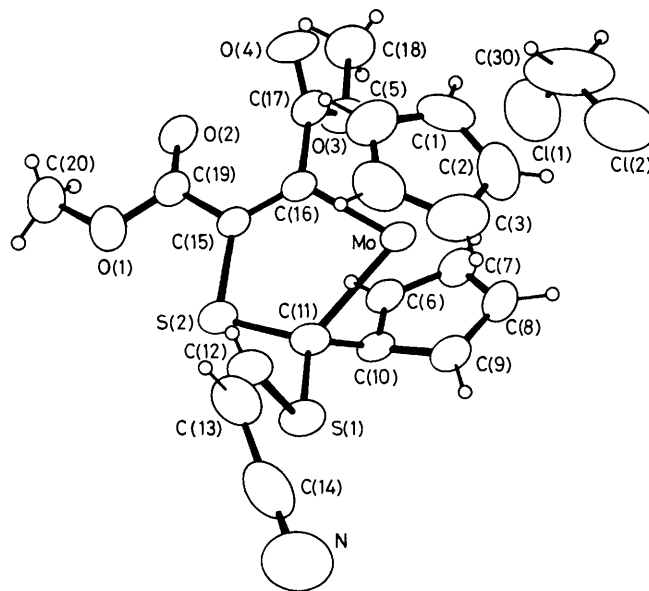


Figure 2. Molecular structure of (5). Selected bond lengths (Å) and angles (°): Mo–C(11) 2.324(4), C(11)–S(2) 1.776(4), S(2)–C(15) 1.762(3), C(15)–C(16) 1.328(5), C(16)–Mo 2.192(4), C(11)–S(1) 1.796(3), C(16)–Mo–C(11) 77.6(2).

complexes and R–C≡C–R; such a species has been postulated only once in rhodium chemistry, from reaction between an Rh–(η^2 -R–C≡C–R) complex and CS₂.²

Employing the complex [Mo(η^5 -C₅H₅)₂(η^2 -CS₂)] (1),³ we now show that reactions of alkynes with η^2 -CS₂ metal

complexes may be much more complicated than previously thought and, particularly, may involve addition of one, two, or three alkynes per M–(η^2 -CS₂) unit.

Hexafluorobut-2-yne reacted with (1) [tetrahydrofuran (thf), room temperature (r.t.), *ca.* 12 h] to give the 1 : 1 adduct (2) in *ca.* 30% yield. The classical type B structure of (2),

deduced from ^{13}C n.m.r. data,[†] was confirmed by an X-ray crystal structure determination.⁴

Reaction of (1) with dimethyl acetylenedicarboxylate (thf, reflux, ca. 5 h) afforded two 1:1 addition compounds: an orange-brown complex (3) (ca. 20% yield) with the type B structure[†] and a dark-green complex (4) (ca. 20% yield), the first fully characterised example of a type C metallacycle^{†‡} (see Scheme 1 and molecular structure in Figure 1).

It has recently been reported that reactions of alkynes with co-ordinated CS_2 can give complexes in which two molecules of alkynes are added to CS_2 .⁵ This is of interest in relation to the recent observation of transition metal catalysed condensation of two molecules of alkynes with CS_2 , CO_2 , or RNCS to give new heterocycles.⁶

Reaction of (3) with cyanoethyne $\text{HC}\equiv\text{C}-\text{CN}$ (CH_2Cl_2 , r.t., ca. 20 h) unexpectedly gave complex (5)[‡] (see Scheme 1 and molecular structure in Figure 2). This reaction, which constitutes a new type of combination of CS_2 with two alkynes, is unique in that it formally involves (i) transformation of a $\eta^5-\text{C}_5\text{H}_5$ ligand into a substituted $\eta^5-\text{C}_5\text{H}_4\text{R}$ group by cleavage of a C-H bond and formation of a C-C bond between the resulting C_5H_4 moiety and the carbon atom of the ex- CS_2 unit and (ii) addition on the unco-ordinated sulphur atom of the alkenyl fragment arising from addition of an H atom onto the alkyne.

Surprisingly, reaction of (1) with $\text{HC}\equiv\text{C}-\text{CN}$ (thf, r.t., ca. 40 h) did not afford an analogue of complexes (5) and (6) but gave compound (7), the first example of a complex in which CS_2 is combined with three molecules of alkynes. The structure of (7) is shown in Figure 3.[‡] Formation of (7) presents the following unusual features: (i) in contrast with the syntheses of (5) and (6), the $\text{Mo}(\eta^5-\text{C}_5\text{H}_5)_2$ fragment remains

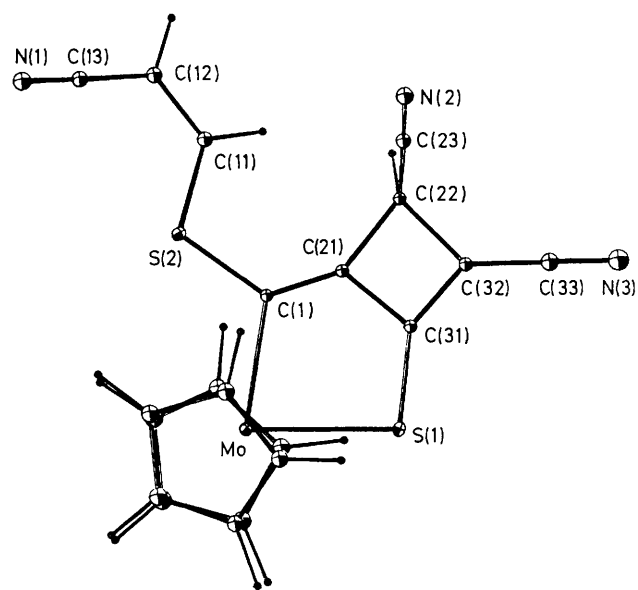


Figure 3. Molecular structure of (7). Selected bond lengths (Å) and angles (°): Mo-C(1) 2.211(13), C(1)-C(21) 1.314(15), C(21)-C(31) 1.443(16), C(31)-S(1) 1.693(12), S(1)-Mo 2.527(4), C(21)-C(22) 1.535(17), C(22)-C(32) 1.539(17), C(32)-C(31) 1.377(17); C(1)-Mo-S(1) 81.0(4).

intact, but there is cleavage of the $\text{M}(\eta^2-\text{CS}_2)$ moiety to give a unit (x); (ii) the unco-ordinated metal sulphur atom bears a (Z)-NC-CH=CH-alkenyl group as in (5) and (6); and (iii) the addition of two alkynes to the C-M-S fragment generates a rather uncommon skeleton which may be viewed as a substituted $\text{C}(21)-\text{C}(22)-\text{C}(32)=\text{C}(31)$ cyclobutene or as a substituted $\text{C}(1)=\text{C}(21)-\text{C}(31)=\text{C}(32)$ butadiene.

The reactions reported here provide unprecedented examples of the reactivity of activated alkynes towards $\eta^2-\text{CS}_2$ metal complexes. They are currently under further investigation, particularly to obtain insights into the mechanisms.

Received, 19th October 1987; Com. 1520

References

- 1 C. Bianchini, C. Mealli, A. Meli, and M. Sabat in 'Stereochemistry of Organometallic and Inorganic Compounds,' Elsevier, Amsterdam, 1986, and references therein.
- 2 Y. Wakatsuki, H. Yamazaki, and H. Iwasaki, *J. Am. Chem. Soc.*, 1973, **95**, 5781.
- 3 G. E. Herberich and J. Okuda, *Chem. Ber.*, 1984, **117**, 3112; J. Okuda, dissertation, Technische Hochschule Aachen, 1984.
- 4 F. Conan *et al.*, in preparation.
- 5 C. Bianchini, C. Mealli, A. Meli, and M. Sabat, *Organometallics*, 1985, **4**, 421; C. Bianchini, C. Mealli, A. Meli, M. Sabat, J. Silvestre, and R. Hoffmann, *ibid.*, 1986, **5**, 1733.
- 6 Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1973, 280; P. Diversi, G. Ingrosso, A. Lucherini, and S. Malquori, *J. Mol. Catal.*, 1987, **40**, 267; T. Tsuda, R. Sumiya, and T. Saegusa, *Synth. Commun.*, 1987, **17**, 147.

[†] Selected ^{13}C n.m.r. data: (100.6 MHz, in CDCl_3) (2) δ 310.3 [Mo-C(S)-S-]; (3) δ 313.1 [Mo-C(S)-S-]; (4) δ 246.7 [Mo-S-C(S)-].

[‡] Crystal data for (4): $\text{C}_{17}\text{H}_{16}\text{MoO}_4\text{S}_2$, $M = 444.38$, triclinic, space group $P\bar{1}$, $a = 7.662(4)$, $b = 14.661(5)$, $c = 15.414(4)$ Å, $\alpha = 96.00(3)$, $\beta = 96.19(3)$, $\gamma = 90.79(4)^\circ$, $U = 1711.3(5)$ Å³, $Z = 4$, $F(000) = 896$, Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu = 9.99$ cm⁻¹, $T = 296$ K. Enraf-Nonius four-circle diffractometer, 6260 measured reflections with $2\theta_{\text{max}} = 54^\circ$, 5030 unique observed reflections, $I > 4\sigma(I)$.

For (5): $\text{C}_{20}\text{H}_{17}\text{MoNO}_4\text{S}_2 \cdot \text{CH}_2\text{Cl}_2$, $M = 580.36$, monoclinic, space group $P2_1/c$, $a = 10.246(4)$, $b = 15.245(9)$, $c = 15.140(8)$ Å, $\beta = 103.89(5)^\circ$, $U = 2296(2)$ Å³, $Z = 4$, $F(000) = 1168$, Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu = 9.9$ cm⁻¹, $T = 296$ K. Enraf-Nonius four-circle diffractometer, 4373 measured reflections with $2\theta_{\text{max}} = 55^\circ$, 3019 unique observed reflections, $I > \sigma(I)$.

For (7): $\text{C}_{20}\text{H}_{13}\text{MoN}_3\text{S}_2$, $M = 455.41$, orthorhombic, space group $Pbca$, $a = 22.089(5)$, $b = 10.699(2)$, $c = 15.660(3)$ Å, $U = 3701(2)$ Å³, $Z = 8$, $F(000) = 1824$, Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu = 9$ cm⁻¹, $T = 293$ K. Enraf-Nonius four-circle diffractometer, 4072 measured reflections with $2\theta_{\text{max}} = 56^\circ$, 1247 unique observed reflections, $I > 4\sigma(I)$.

The structures were solved by the heavy atom method (Patterson, Fourier) and refined by least-squares. Final residuals were R 0.038, 0.041, and 0.059, for (4), (5), and (7), respectively.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.