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Incorporation of alkyne and vinylidene ligands into tetrazolate groups at a sulfur-rich dimolybdenum site using sodium azide

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Dedicated to Dr Pierre Braunstein in recognition of his many and outstanding contributions to organometallic chemistry.

Abstract

Treatment of either the μ-alkyne complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}PhCCH)](BF_4)$ (**1**) or the μ-vinylidene derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}(CCHR)](BF_4)$ (**2**) (R = Ph, Tol, *n*Pr, $C(CH_3)=CH_2$) with NaN_3 in ethanol at room temperature readily afforded μ-tetrazolate carbene complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3)\{\mu\text{-}\eta^1(C){:}\eta^1(N)\text{-}N_4CCR)\}]$ (R = Ph (**4a**), Tol (**4b**), *n*Pr (**4c**), $C(CH_3)=CH_2$ (**4d**)). A mechanism which accounts for the formation of **4** by intramolecular 1,3-dipolar cycloaddition of metal-coordinated azide ligands to metal-coordinated nitriles is discussed. The structure of complex **4a** has been determined by single X-ray diffraction analysis.

Keywords: Azides; μ-Tetrazolate complexes; Carbenes; 1,3 Cycloaddition; Dimolybdenum complexes; Thiolate compounds

1. Introduction

Tetrazole derivatives frequently exhibit significant biological activity and, in consequence, have found a wide variety of applications as active heterocycles in pharmacy, medicine and agriculture [1]. Two main types of reaction have been used in their synthesis. One involves [2+3] cycloaddition between organonitriles and azides, such as the salt NaN_3 or silyl, aliphatic, or aromatic azides RN_3 [2]. The other proceeds by alkylation of tetrazole anions and has the drawback that mixtures of N(1)- and N(2)-alkylation isomers are often obtained [3]. More recently it has been demonstrated that the involvement of metal ions allows azides to add to nitriles under milder conditions [4–6]. For example, the regio-specific synthesis of 5-substituted 2-allyl-tetrazoles via palladium-catalyzed reactions of alkyl- and arylidenemalononitriles, allylic acetates and trimethylsilyl azide has just been reported [7].

The known metal complexes of unsubstituted and substituted tetrazoles have been obtained by various routes. A well known path to these derivatives lies in complexing the metal to neutral [8] or anionic [9] tetrazoles. However, 1,3-dipolar cycloaddition reactions of organonitriles [5c,10] or isocyanides [5a,5b,5d,11] to the azide ligand of a metal complex have proved even more popular and have received considerable attention. Tetrazolato-complexes are also conveniently obtained by the facile attack of azide ion on coordinated nitriles through a 1,3-dipolar cycloaddition reaction [12]. Recently, a novel route to tetrazolato-complexes, involving reactions of ruthenium cyclopropenyl compounds with trimethylsilyl azide, has been described [13]; it proceeds by successive formation of vinylidene and N-coordinated nitrile intermediates; a [2+3] cycloaddition of the C≡N bond to another azide anion followed by metal migration is proposed as the final step [13].

Alkynes and their thermodynamically less stable vinylidene isomers are among the strongest π-acceptor

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ligands in organometallic chemistry. They are therefore good candidates for reaction with nucleophilic azido-species. Accordingly, we decided to treat these unsaturated ligands with sodium azide, hoping both to obtain new tetrazolato-complexes under mild conditions and to gain further insight into the modes of coordination of tetrazoles. Since the cyclic tetrazolato(−1) anion is isoelectronic with the cyclopentadienyl anion it may reasonably be expected to display several different bonding modes in coordination compounds. First, it could act as an η^5 π-bonding ligand; however, only two examples of this mode of coordination have been established, one from IR evidence [9d] and the other by a crystallographic study [9e]. Secondly, the carbon atom of the ring can form a σ-bond to the metal when the tetrazole ligand is the result of cycloaddition of isocyanide to metal-coordinated azide 5a,5b,5c,12. In all other cases, whether they involve cycloaddition of organic nitrile to coordinated azide or of azide to coordinated nitrile, N-coordinated tetrazolato-compounds are obtained as a mixture of isomers in which different tetrazolate ring nitrogen atoms are attached to the metal [10,12].

A survey of transition metal tetrazolato-complexes formed from cycloaddition reactions reveals that they involve only Au(III), Pd(0), Pd(II), Pt(0), Pt(II), Co(III), Rh(III), Ir(0) and Ru(II). To the best of our knowledge, none of the earlier transition metals has till now been shown to take part in such a cycloaddition reaction. Accordingly, we chose a group 6 synthon, the sulfur-rich dimolybdenum $\{Cp_2Mo_2(\mu\text{-}SMe)_3\}$ system, for the preparation of new tetrazolato-compounds. We now report on the reactions of both the μ-alkyne dimolybdenum complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}PhCCH)]$ (BF_4) (**1**) and of the μ-vinylidene species $[Mo_2Cp_2(\mu\text{-}SMe)_3$ $(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHR)]$ (BF_4) (**2**) [14] with sodium azide. We shall show that the reaction of **1** involves the vinylidene species **2** as intermediate and that, in consequence, the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}^+$ system allows an unprecedented multistep activation in which the starting alkyne is ultimately incorporated into a substituted tetrazole.

2. Experimental

2.1. Materials and methods

All reactions were performed under an atmosphere of argon or dinitrogen using conventional Schlenk techniques. Solvents were deoxygenated and dried by standard methods. The starting materials $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}PhCCH)]$ (BF_4) (**1**) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHR)]$ (BF_4) (R = Ph (**2a**), Tol (**2b**), *n*Pr (**2c**), $C(CH_3){=}CH_2$ (**2d**)) were prepared as described previously [14]. All other reagents were purchased commercially. Yields of all products are relative to the starting dimolybdenum complexes. Column chromatography was carried out with silica gel purchased from SDS. Chemical analyses were performed either by the Service de Microanalyse I.C.S.N., Gif sur Yvette, France or by the Océanographie Chimique Laboratory at the University of Brest. The mass spectra were measured with a GC/MS Ribermag $R_{10\text{-}10}$ spectrometer at the Laboratoire de Biochimie, Faculté de Médecine (Brest, France). IR spectra were recorded on a Nicolet-Nexus FT IR spectrometer from KBr pellets. The NMR spectra (^1H, ^{13}C), in $CDCl_3$ or CD_2Cl_2 solutions, were recorded at room temperature with a Bruker AC 300 or AMX_3 400 spectrometer and were referenced to $SiMe_4$. ^1H–^1H 2D-COSY and ^1H–^{13}C 2D-HMBC and HMQC spectra were recorded on a Bruker 500 and AMX_3 400 spectrometers.

2.2. Syntheses of $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1(C){:}\eta^1(N)\text{-}(N_4CCR)\}]$ (R = Ph (**4a**), Tol (**4b**), *n*Pr (**4c**), $C(CH_3){=}CH_2$ (**4d**))

2.2.1. Method A

In a typical procedure a solution of complex **2** (200 mg, ≈0.31 mmol) in ethanol (20 ml) was stirred in the presence of 2 equiv. of NaN_3 (≈41 mg, ≈0.62 mmol) for 30 min at room temperature. The colour of the solution readily turned from green to yellow–brown. The solvent was then removed under vacuum and the organometallic products were extracted with hot (80 °C) toluene (2 × 50 ml). After evaporation of the toluene, the residue was dissolved in CH_2Cl_2 (5 ml) and chromatographed on silica gel. Elution with CH_2Cl_2 (CH_2Cl_2:THF(99:1) when R = Tol) afforded a greenish band, which gave **3** as brown solids (17% (R = Ph), 31% (R = Tol), 16% (R = *n*Pr), 28% (R = $C(CH_3){=}CH_2$)). Further elution with CH_2Cl_2/ethanol (9.5:0.5) removed a brown band. After evaporation of the volatiles, the residues were washed with pentane (5 ml) to afford complexes **4** as analytically pure yellow–brown solids. These complexes **4** were obtained as mixtures of two isomers (**4_1** and **4_2**), except for **4d** (R = $C(CH_3){=}CH_2$) which was a mixture of four isomers (**$4d_{1a}$**, **$4d_{1b}$**, **$4d_{2a}$** and **$4d_{2b}$**).

Compound **4a** (74% yield): IR bands attributed to the tetrazolate ring at 1700–400 cm^{-1} region (KBr pellets): 1644m, 1480m, 1399m, 1298m, 1146m, 1069m, 1020w, 997w, 933m, 851m, 703m, 650w cm^{-1}. ^1H NMR (CD_2Cl_2, ppm), δ (**4_{a1}**): 7.36 (m, J_{HH}=8.0 Hz, 2H, Ph), 7.19 (*p*-t, J_{HH}=7.6 Hz, 1H, Ph), 6.74 (d, J_{HH}=7.4 Hz, 1H, Ph), 6.63 (d, J_{HH}=8.0 Hz, 1H, Ph), 5.74 (s, 5H, Cp), 5.62 (s, 5H, Cp), 1.95 (s, 3H, SMe), 1.60 (s, 3H, SMe), 1.27 (s, 3H, SMe); δ (**4_{a2}**): 7.36 (m, J_{HH}=8.0 Hz, 2H, Ph), 7.19 (p-t, J_{HH}=7.6 Hz, 1H, Ph), 6.67 (d, J_{HH}= 7.4 Hz, 1H, Ph), 6.61 (d, J_{HH}=8.0 Hz, 1H, Ph), 5.77 (s, 5H, Cp), 5.70 (s, 5H, Cp), 1.54 (s, 3H, SMe), 1.34 (s, 5H, Cp), 1.30 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR(CD_2Cl_2, ppm), δ

(**4a$_1$**): 294.7 (Mo*C*), 174.0 (*C*N$_4$), 159.2 (C_{ipso}, Ph), 127.1, 122.35, 122.15 (Ph), 100.15 (C_5H_5), 95.0 (C_5H_5), 18.5 (S*C*H$_3$), 15.4 (S*C*H$_3$), 13.2 (S*C*H$_3$); δ (**4a$_2$**): 293.75 (Mo*C*), 173.2 (*C*N$_4$), 159.65 (C_{ipso}, Ph), 127.35, 123.1, 122.3 (Ph), 100.2 (C_5H_5), 95.7 (C_5H_5), 16.2 (S*C*H$_3$), 15.65 (S*C*H$_3$), 14.2 (S*C*H$_3$). Mass spectrum: *m*/*z* 621 (M^+). *Anal*. Calc. for $Mo_2C_{21}H_{24}N_4S_3$: C, 40.6; H, 3.90; N, 9.0. Found C, 40.3; H, 3.77; N, 8.9%.

Compound **4b** (69% yield): IR bands attributed to the tetrazolate ring at 1700–400 cm^{-1} region (KBr pellets): 1627br, 1450sh, 1392m, 1329w, 1293mw, 1260mw, 1143m, 1063m, 1043m, 997sh, 940mw, 849sh, 694w, 520mw, 473w cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm), δ (**4b$_1$**): 7.14 (d, J_{HH}=9.0 Hz, 1H, Tol), 7.11 (d, J_{HH}=9.0 Hz, 1H, Tol), 6.66 (d, J_{HH}=7.1 Hz, 1H, Tol), 6.51 (d, J_{HH}=7.1 Hz, 1H, Tol), 5.74 (s, 5H, Cp), 5.63 (s, 5H, Cp), 2.36 (s, br., 3H, CH$_3$–Tol), 1.92 (s, 3H, SMe), 1.57 (s, 3H, SMe), 1.27 (s, 3H, SMe); δ (**4b$_2$**): 7.14 (d, J_{HH}=9.6 Hz, 1H, Tol), 7.11 (d, J_{HH}=9.6 Hz, 1H, Tol), 6.55 (d, J_{HH}=7.2 Hz, 1H, Tol), 6.50 (d, J_{HH}=7.2 Hz, 1H, Tol), 5.76 (s, 5H, Cp), 5.70 (s, 5H, Cp), 2.36 (s, br, 3H, CH$_3$–Tol), 1.52 (s, 3H, SMe), 1.35 (s, 3H, SMe), 1.32 (s, 3H, SMe). ^{13}C{^{1}H} NMR($CDCl_3$, ppm), δ (**4b$_1$**): 296.1 (Mo*C*), 173.1 (*C*N$_4$), 156.0 (C_{ipso}, Tol), 134.4, 129.4, 127.5, 122.4, 121.4 (*C* Tol), 99.6 (C_5H_5), 94.6 (C_5H_5), 21.2 (*C*H$_3$–Tol), 18.5 (S*C*H$_3$), 15.2 (S*C*H$_3$), 12.6 (S*C*H$_3$); δ(**4b$_2$**): 295.4 (Mo*C*), 171.5 (*C*N$_4$), 156.4 (C_{ipso}, Tol), 134.6, 127.9, 121.6, 121.5 (*C* Tol), 99.9 (C_5H_5), 95.5 (C_5H_5), 21.1(*C*H$_3$–Tol), 16.3 (S*C*H$_3$), 25.8 (S*C*H$_3$), 13.2 (S*C*H$_3$). *Anal*. Calc. for $C_{22}H_{26}Mo_2N_4S_3$: C, 41.7; H, 4.13; N, 8.8. Found: C, 42.1; H, 4.35; N, 8.1%.

Compound **4c** (80% yield):IR bands attributed to the tetrazolate ring at 1700–400 cm^{-1} region (KBr pellets): 1629m, 1466mw, 1387s, 1293m, 1260m, 1149m, 1057s, 1031m, 938m, 849m, 695w, 520mw cm^{-1}. ^{1}H NMR($CDCl_3$, ppm), δ (**4c$_1$**): 5.89 (s, 5H, Cp), 5.56 (s, 5H, Cp), 3.56 (m, 2H, –C*H*$_2$–CH$_2$CH$_3$), 1.86 (s, 3H, SMe), 1.54 (s, 3H, SMe), 1.25 (t, J_{HH}=7.0 Hz, 2H, –CH$_2$–*CH*$_2$–CH$_3$), 1.09 (t, J_{HH}=7.0 Hz, 3H, –CH$_2$–CH$_2$–C*H*$_3$), 1.00 (s, 3H, SMe); δ (**4c$_2$**): 5.93 (s, 5H, Cp), 5.65 (s, 5H, Cp), 3.63 (m, 2H, –C*H*$_2$–CH$_2$–CH$_3$), 1.50 (m, 2H, –CH$_2$–C*H*$_2$–CH$_3$), 1.48 (s, 3H, SMe), 1.12 (t, J_{HH}=7.2 Hz, 3H, –CH$_2$–CH$_2$–C*H*$_3$), 1.09 (s, 3H, SMe), 1.08 (s, 3H, SMe). ^{13}C{^{1}H} NMR ($CDCl_3$, ppm), δ (**4c$_1$**): 307.3 (Mo*C*), 173.3 (*C*N$_2$), 98.45 (C_5H_5), 94.5 (C_5H_5), 55.15 (–*C*H$_2$–CH$_2$–CH$_3$), 26.15 (–CH$_2$–*C*H$_2$–CH$_3$), 18.65 (S*C*H$_3$), 15.5 (S*C*H$_3$), 15.05 (–CH$_2$–CH$_2$–*C*H$_3$), 14.05 (S*C*H$_3$); δ (**4c$_2$**): 305.7 (Mo*C*), 172.8 (*C*N$_2$), 98.75 (C_5H_5), 95.2 (C_5H_5), 55.5 (–*C*H$_2$–CH$_2$–CH$_3$), 25.8 (–CH$_2$–*C*H$_2$–CH$_3$), 16.4 (S*C*H$_3$), 16.05 (S*C*H$_3$), 14.7 (–CH$_2$–CH$_2$–*C*H$_3$), 14.4 (S*C*H$_3$). *Anal.* Calc. for $C_{18}H_{26}Mo_2N_4S_3$. 0.25 CH_2Cl_2: C, 36.1; H, 4.39; N, 9.2. Found: C, 36.0; H, 4.44; N, 8.2%.

Compound **4d** (72% yield): IR bands attributed to the tetrazolate ring at 1700–400 cm^{-1} region (KBr pellets): 1617m, 1450w, 1396m, 1344 mw, 1294m, 1258 mw, 1135w, 1044m, 1017m, 931m, 861s, 723mw, 553w, 464w cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm), δ (**4d$_{1a}$**, **4d$_{1b}$**): 5.89, 5.88 (2s, 2 × 5H, 2Cp), 5.59 (s, 10H, 2Cp), 4.85 (s, 2H, CH_2=CMe), 4.11 (s, 2H, CH_2=CMe), 1.87, 1,86 (2s, 2 × 3H, 2CH$_2$=C(CH_3)), 1.56, 1.54 (2s, 2 × 3H, 2SMe), 1.18, 1.17 (2s, 2 × 3H, 2SMe), 1.11, 1.06 (2s, 2 × 3H, 2SMe);δ (**4d$_{2a}$**, **4d$_{2b}$**): 5.93, 5.92 (2s, 2 × 5H, 2Cp), 5.67 (s, 10H, 2Cp), 4.87, 4.86 (2s, 2H, 2CH_2=CMe), 4.16, 4.12 (2s, 2H, 2CH_2=CMe), 2.02, 1.99 (2s, 2 × 3H, 2CH$_2$=C(CH_3)), 1.52, 1.50 (2s, 2 × 3H, 2SMe), 1.22, 1.20 (2s, 2 × 3H, 2SMe), 1.15, 1.13 (2s, 2 × 3H, 2SMe). ^{13}C{1H} NMR ($CDCl_3$, ppm), δ(**4d$_{1a}$**, **4d$_{1b}$**): 170.95 (s, *C*N$_2$), 160.25 (s,*C*(Me)=CH$_2$), 104.15 (s, *C*H$_2$=C(Me)), 99.7 (s, C_5H_5), 94.65, 94.6 (2s, C_5H_5), 25.5 (s,CH$_2$=C(*C*H$_3$)), 16.05 (s, S*C*H$_3$), 14.05 (s, S*C*H$_3$); δ (**4d$_{2a}$**, **4d$_{2b}$**): 298.45, 298.3 (2s, Mo*C*), 170.35, 170.3 (2s, *C*N$_2$), 160.7, 160.65 (2s,CH$_2$=*C*(Me)), 104.8, 104.75 (2s,*C*H$_2$=CMe)), 100.1, 100.95 (2s, C_5H_5), 95.45, 95.4 (2s, C_5H_5), 25.35 (s, CH$_2$=C(*C*H$_3$)), 16.65, 16.2 (2s, S*C*H$_3$), 15.5, 15.1 (2s, S*C*H$_3$), 14.9, 13.9 (2s, S*C*H$_3$). *Anal*. Calc. for $C_{18}H_{24}Mo_2N_4S_3$: C, 37.0; H, 4.14; N, 9.6. Found: C, 37.2; H, 4.28; N, 8.7%.

2.2.2. Method B

To a solution of the μ-alkyne complex [Mo_2Cp_2(μ-SMe)$_3$(μ-PhCCH)][BF_4] (**1**) in ethanol (20 ml) was added 2 equiv. of NaN_3 (40 mg, 0.62 mmol). The solution was stirred for 30 min at room temperature and the subsequent procedure was similar to *Method A*. Two products **3a** and **4a** were characterised by ^{1}H NMR. Yields: **3a** (R = Ph), 6%; **4a** (R = Ph), 61%.

2.3. X-ray structure analysis of [Mo_2Cp_2(μ-SMe)$_3${μ-η^1(C): η^1(N)-(N_4CCPh)}] (**4a**)

2.3.1. Crystal data

$C_{21}H_{24}Mo_2N_4S_3\cdot CH_2Cl_2$, formula weight 705.43, orthorhombic, space group $P2_12_12_1$, a = 7.5964(3), b = 15.7764(8), c = 23.1438(9) Å, V = 2773.6(2) Å^3, Z = 4, ρ = 1.689 g cm^{-3}, μ = 1.341 mm^{-1}, F(0 0 0) = 1408.

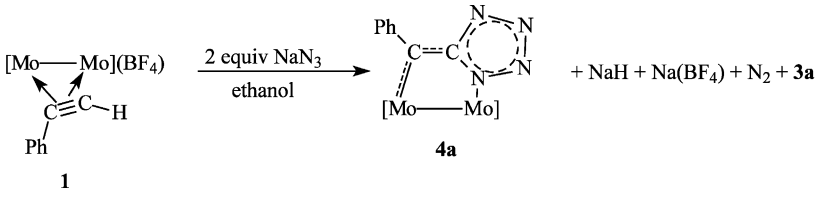
Single crystals suitable for X-ray analysis were obtained from a CH_2Cl_2–pentane (1:4) solution. All crystallographic measurements were made on a Nonius KappaCCD diffractometer with Mo Kα radiation, λ = 0.70173 Å, at 100 K. Transmission factors based on Gaussian quadrature for the plate-shaped crystal of dimensions 0.28 × 0.11 × 0.04 mm^3 were in the range 0.948–0.705. 15 218 Measurements yielded 8204 unique intensities (R_{int} = 0.084), comprising 95.2% of the independent reflections with θ(Mo Kα) ≤ 32°. These were used in the least-squares refinements on F^2 with weights chosen to give a goodness-of-fit near unity. Apart from four molecules of **4a** the unit cell also contains four disordered CH_2Cl_2 molecules whose scattering was accounted for non-parametrically [15]. For 8204 reflec-

tions, including 3043 Friedel pairs, $R(F) = 0.074$, $wR(F^2) = 0.125$, $|\Delta\rho| < 1.5$ e Å^{-3} after adjustment of 274 parameters. The Flack parameter $x = 0.02(6)$ confirms the correctness of the absolute structure [16].

3. Results and discussion

3.1. Syntheses and spectroscopic characterization of (tetrazolato) complexes (4). Molecular structure of [$Mo_2Cp_2(\mu$-SMe)$_3\{\mu$-η^1(C): η^1(N)-(N_4CCPh)}] (4a)

Treatment of the μ-alkyne complex [$Mo_2Cp_2(\mu$-SMe)$_3(\mu$-PhCCH)] (BF_4) (**1**) with 2 equiv. of NaN_3 in ethanol at room temperature gave good yields of the tetrazolato-compound [$Mo_2Cp_2(\mu$-SMe)$_3\{\mu$-η^1(C): η^1(N)-(N_4CCPh)}] (**4a**) within 30 min (Eq. (1)) together with the μ-acetylide complex [$Mo_2Cp_2(\mu$-SMe)$_3(\mu$-η^1:η^2-C≡CPh)] (**3a**). These complexes were extracted with toluene from the residue left after evaporation of the ethanolic solution and thus were easily separated from the insoluble matter, namely NaH and Na(BF_4). **4a** was separated from **3a** by column chromatography and isolated as a spectroscopically and analytically pure brownish powder in approximately 60% yield.



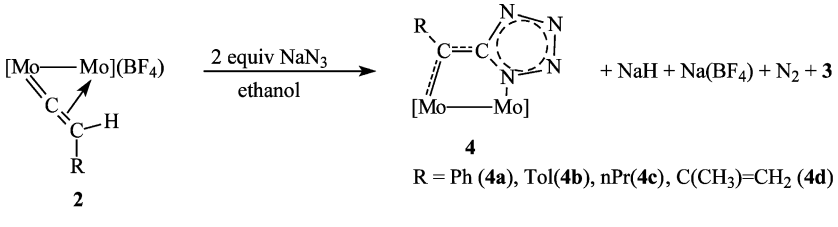
(1)

Under identical conditions treatment of [$Mo_2Cp_2(\mu$-SMe)$_3(\mu$-η^1:η^2-C=CHR)](BF_4) (**2**) with NaN_3 also led to the addition of four nitrogen atoms, readily affording the brown tetrazolate complexes [$Mo_2Cp_2(\mu$-SMe)$_3\{\mu$-η^1(C):η^1(N)-N_4CCR)}] (**4**) (R = Ph (**4a**), Tol (**4b**), *n*Pr (**4c**), C(CH_3)=CH_2 (**4d**)) in good yields (69–80%) (Eq. (2)) together with μ-acetylide compounds [$Mo_2Cp_2(\mu$-SMe)$_3(\mu$-η^1:η^2-C≡C–R)] (**3**) (16–31% yields). From the reaction mixture Na(BF_4) and NaH were separated off using toluene, in which there are insoluble, and Na(BF_4) was identified by IR spectroscopy.

The μ-acetylide complexes **3** formed as by-products of these reactions were characterised by comparing their spectra with those of authentic samples [14]. Ready deprotonation of **1** and **2** by azide is consistent with their known reactions with other bases [14].

Complexes **4** are thermally stable in the solid state and in solution and were characterised analytically and from mass, infrared, and multinuclear (^{1}H and ^{13}C) NMR spectroscopic data given in Section 2. It is immediately apparent from their spectra that complexes **4a**–**4d** have the same basic structure. As expected, the IR spectra of **4a**–**4d** are almost identical, showing characteristic bands for the η^5-Cp groups at approximately 1420, 1010 and 820 cm^{-1}. For compound **4a**, the bands near 1590, 1110, 801 and 650 cm^{-1} were assigned to stretching and bending modes of the phenyl group. For each compound **4** bands arising from ring breathing, ring deformation and out-of-plane ring bending vibrations of a typical tetrazolate group [17] appear at about 1630, 1460, 1360, 1335, 1295, 1260, 1150, 1060, 1040, 980, 930, 850, 690 and 450 cm^{-1}. Discussion of the NMR data is deferred until the molecular structure of **4a** obtained by X-ray diffraction (Table 1) has been described.

Molecules of **4a** (Fig. 1) contain a bidentate tetrazolate ligand: it coordinates to Mo1 through C4, which is also attached to the carbon of the tetrazole ring, and



(2)

to Mo2 through N9. This is an unprecedented bonding mode for the tetrazolate ligand. Known examples of bridging tetrazolate ligands either use the nitrogen atoms at the 1-, 2- and 3-positions to bridge and chelate the metal atoms [8e,18] or are of the η^2 type, with the two nitrogens opposite the carbon [9d,10a] or the two nitrogens at the 1-, 2-positions [8c] taking part in bonding. The N_4C tetrazole ring is planar to within experimental error; Mo1, Mo2, C4 and C31 lie close to the plane of the ring, with Mo1 showing the largest displacement (0.125(1) Å). The ring C–N and N–N bond lengths indicate strong π-electron delocalization.

If the Mo1–C4 bond is regarded as carbene-like in nature, a count of 18 electrons is reached around Mo1. There is extensive electron delocalization along the Mo1–C4–C5 chain, as shown by the shortness of the Mo1–C4 and C4–C5 bonds (2.048(5) and 1.455(7) Å). The orientation of the phenyl ring (C32–C31–C4–C5 = 90(1)°] and the length of the C4–C31 bond (1.494(7) Å) indicate that there is no π-overlap across C4–C31. The Mo(2)–N(9) distance (2.141(5) Å) implies a bond order close to unity; it is similar to the value of 2.151(2) Å in the μ-amido complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ [19], but longer than that of 2.058(5) Å in $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N{=}NMe)]$ [20] and much longer than the terminal Mo–N distance of 1.809(3) Å in $[Mo\{N(CH_2CH_2S)_3\}(NNMe)]$ [21].

The Mo–Mo distance (2.7913(6) Å) also indicates a bond of unit order as required by electron counting rules; it is longer than the values of 2.719(2), 2.709(1), 2.613(1) and 2.564(1) Å found, respectively, in $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1(O):\eta^1(N)\text{-}OC(Me)NH\}]$ [22], $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}O_2CCF_3)]$ [23], $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^2\text{-}N{=}NMe)]$ [20] and $[MoCp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}N{=}CHCH_3)]$ [24]. In all of these complexes a fourth ligand bridges a $Cp_2Mo_2^{III}(\mu\text{-}SMe)_3$ unit and each Mo atom has a distorted piano-stool coordination. In **4a** the atoms Mo1, S1, S2 and Mo2 are, in consequence, almost coplanar (torsion angle 169.5(1)°) and the isomer present in the solid has an *anti*-configuration of the methyl groups attached to S1 and S2. The higher *trans*-influence of C4 compared with N9 atom is evident from the lengthening of Mo1–S3 relative to Mo2–S3.

Table 1
Selected bonds distances (Å) and angles (°) of **4a**·CH_2Cl_2

Bond distances			
Mo(1)–C(4)	2.048(5)	Mo(2)–S(3)	2.4279(14)
Mo(1)–S(1)	2.4612(14)	C(4)–C(5)	1.455(7)
Mo(1)–S(2)	2.4841(13)	C(4)–C(31)	1.494(7)
Mo(1)–S(3)	2.4997(13)	C(5)–N(6)	1.351(7)
Mo(1)–Mo(2)	2.7913(6)	C(5)–N(9)	1.357(7)
Mo(2)–N(9)	2.141(5)	N(6)–N(7)	1.330(7)
Mo(2)–S(1)	2.4203(14)	N(7)–N(8)	1.342(7)
Mo(2)–S(2)	2.4593(14)	N(8)–N(9)	1.341(6)
Bond angles			
Mo(1)–C(4)–C(5)	121.3(4)	C(4)–C(5)–N(9)	123.0(5)
Mo(1)–C(4)–C(31)	128.7(4)	N(6)–C(5)–N(9)	110.5(5)
C(31)–C(4)–C(5)	110.1(4)	N(8)–N(9)–C(5)	106.1(4)
C(4)–C(5)–N(6)	126.4(5)		

E.s.d.s are given in parentheses, see Fig. 1 for atomic numbering.

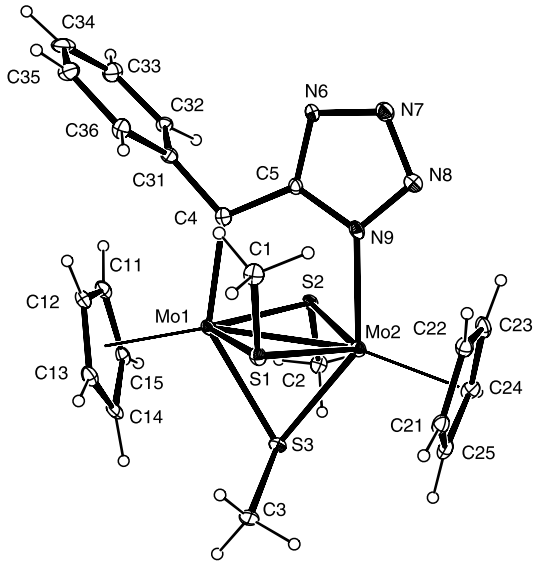


Fig. 1. An ORTEP representation of the structure of [Mo2Cp2(μ-SMe)$_3${μ-η^1(C): η^1(N)-(N4CCPh)}] (**4a**) at 20% probability showing the atom labelling scheme.

Having considered the crystal structure of **4a**, we now turn to the spectroscopic data for all the complexes **4**. First, it is apparent that the solution structures are consistent with that observed in the solid state for **4a**. However, it was shown by multinuclear NMR spectroscopy that in solution all of the complexes, except **4d**, are present in two interconvertible isomeric forms, $\mathbf{4_1}$ and $\mathbf{4_2}$, which differ only in the orientations (*syn* or *anti*) of the bridging SMe groups. These isomers were inseparable by conventional chromatographic techniques and were obtained in variable ratio according to the thermal treatment of the crude products: the longer the solution was heated the lower the yield of $\mathbf{4_1}$. The ^{1}H NMR spectra of compounds **4** exhibited the sets of resonances expected for the $[Mo_2Cp_2(\mu\text{-}SMe)_3]$ core and for the R groups. The tetrazolato-vinylidene bridge μ-η^1(C):η^2(N)-$C_\alpha{=}C_\beta(N_4)$ was characterised in the $^{13}C\{^1H\}$NMR spectra by the observation of two resonances, at low field in the carbene ($\approx$300 ppm) and in the vinyl-cyanide ($\approx$172 ppm) ranges, which were assigned to C_α and C_β, respectively. As expected from their structural inequivalence, separate resonances were observed for the two C_5H_5 groups.

The ^{1}H and ^{13}C NMR spectra of **4d**, $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1(C):\eta^1(N)\text{-}N_4CCR\}]$ where R is the vinyl group $-C_\alpha'(Me){=}C_\beta'H_2$, indicate the presence of four interconverting isomers. These arise because the methyl groups on the bridging sulfur atoms can be either *syn* or

anti; in each of these arrangements the methyl group attached to C'_α in the $N_4C–C–C'_\alpha(Me)=C'_\beta H_2$ ligand can be either *cis* or *trans* to the carbon atom of the tetrazolate ring. The coupling pattern for the methyl and methylene protons of the vinyl groups of **4d** was determined from a 2D-COSY NMR experiment which allowed assignment of the resonances at δ 2.02 and 1.99 to the methyl groups of the vinyl unit of the major isomer **4d$_2$**. The respective assignment of the three sets of carbon peaks observed at approximately 25.3, 104.8 and 160.7 ppm (**4d$_2$**) to the methyl group attached to C'_α, to the $C'_\beta H_2$ methylene group and to C'_α was readily accomplished via $^1H–^{13}C$ 2D HMQC and HMBC experiments. It is obvious from the $^1H–^{13}C$ 2D HMQC spectra that methylene protons ($\delta \approx 4.8$ and 4.1) are coupled (J_{CH}) to carbon at approximately 104.8 ppm, whereas the methyl protons (δ 2.02 and 1.99) are correlated with the carbon atom at approximately 25.3 ppm. The correlation peak between the methylene protons at approximately 4.8 and 4.1 ppm and the carbon atom at approximately 160.7 ppm ($^2J_{CH}$) allowed the assignment of this resonance to the $C_{\alpha'}$ carbon atom.

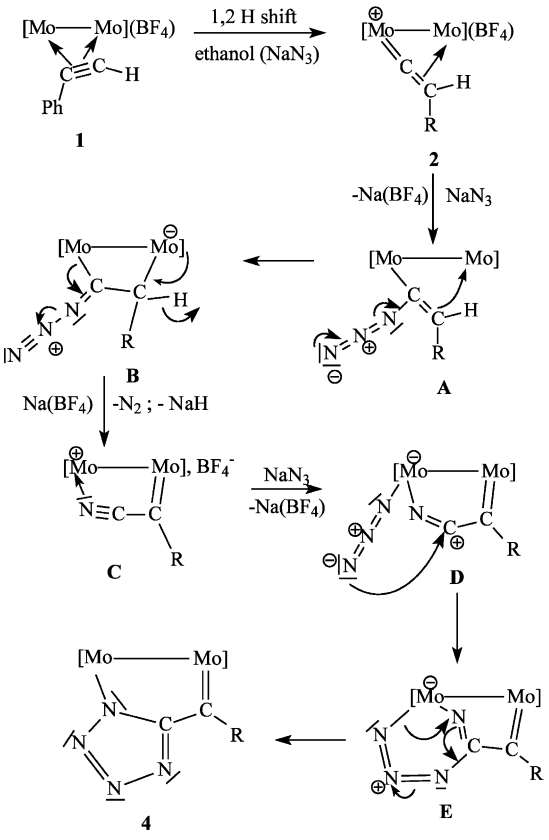
Full assignment of the proton chemical shifts observed for the *n*-propyl ($–C_\gamma H_2–C_\beta H_2–C_\alpha H_3$) group in the ^1H NMR spectra of **4c$_2$** was achieved by means of $^1H–^1H$ 2D-COSY NMR experiments. These spectra showed correlations between the two CH_2 and the CH_3 groups, which allowed the attribution of the resonances at 1.12, 1.50 and 3.63 ppm to the protons of the $C_\alpha H_3$, $C_\beta H_2$ and $C_\gamma H_2$ units, respectively. In other respects $^1H–^{13}C$ HMBC 2D experiments also allowed full assignment of resonances due to the carbons of the *n*-propyl group. The correlation peaks between the methyl protons at 1.12 ppm and both C_β(δ 25.78) ($^2J_{CH}$) and C_γ(δ 55.52) ($^3J_{CH}$), those between the protons of the CH_2 group at 1.50 ppm and C_γ at 55.52 ppm ($^2J_{CH}$), and, finally, those between the protons of the CH_2 unit at 3.63 ppm and three carbon atoms, C_β at 25.78 ppm ($^2J_{CH}$), the carbene atom at 305.71 ppm ($^2J_{CH}$) and the carbon atom of the tetrazole ring at 172.80 ppm ($^3J_{CH}$), are in accord with a $C_\alpha H_3–C_\beta H_2–C_\gamma H_2–C(=Mo)–CN_4$ backbone.

3.2. Discussion and mechanistic considerations

We have shown that addition of NaN_3 to an ethanolic solution of either the μ-alkyne complex **1** or the μ-vinylidene derivatives **2** led readily to the tetrazolato-bridged bis(η-cyclopentadienylmolybdenum) compounds **4**. In both cases significant amounts of μ-acetylide derivatives **3** were obtained as minor products, resulting in a reduction of the yields of **4** to 61–80%. To show that **1** and **2** were deprotonated, at least partly, by N_3^- to give **3**, before reaction with sodium azide produced **4**, we added excess (5 equiv.) Me_3SiN_3 to a tetrahydrofuran solution of **2a**. No reaction was observed under the conditions used above for synthesising **4** by reacting **1** or **2** with NaN_3. However, when the tetrahydrofuran solution was heated (66 °C) for 12h **4a** was obtained, but not the μ-acetylide complex **3a**. This observation implies that, unlike sodium azide, Me_3SiN_3 does not readily form the base N_3^- for the deprotonation of **1** and **2a**. Addition of an ethanolic solution of the μ-acetylide compound **3a** to that of NaN_3 at room temperature gave **4a** only in very low yield (9%), after stirring the solution for 30 min. It is thought that the μ-tetrazolate complex, which was formed in this reaction, resulted from slow protonation of **3a** in ethanol, giving the μ-vinylidene compound **2a** which in its turn was transformed into **4a** in the presence of NaN_3. Thus, unlike the μ-alkyne **1** and μ-vinylidene **2** complexes the μ-acetylide derivatives **3** did not react with sodium azide to give N-tetrazolate species **4**.

These results indicate that the reactions of **1** and **2** with NaN_3 are not simple processes in that they involve the addition of two azido anions. We also note that treatment of **1** or **2** with 2 equiv. of NaN_3 under 1 atm. of dinitrogen did not afford **4** in higher yields than those obtained when the reaction was carried out under argon. Evidently dinitrogen is not a participant in these reactions and azide is the sole source of the nitrogen atoms present in the tetrazole ring.

Scheme 1 shows a reaction path consistent with the above observations which are not, we concede, complete enough yet to define all the elementary steps involved. The initial step is the 1,2-shift of the hydrogen in the μ-alkyne **1**, promoted by the presence of NaN_3 in ethanol, to give the μ-vinylidene **2**. This known reaction [14] provides a common path from **1** or **2** to **4** which was obtained in similar yields irrespective of whether **1** or **2** was the starting complex. Nucleophilic addition of azide at C_α of the vinylidene ligand next gives the alkenyl intermediate **A**. The electrophilic character of the α-carbon atom of vinylidene ligands [25] is established, as its susceptibility to azide attack [13,26]. Subsequent internal rearrangement gives the μ-alkyl derivative **B** which then loses both N_2 and alkyl hydrogen (in the form of NaH), giving the N-coordinated cationic intermediate **C**. Mononuclear complexes of ruthenium provide a precedent for the existence of such intermediates [13]. **C** contains an electrophilic molybdenum atom which can be attacked by a second azide anion to afford **D**. Formation of **E** and then **4** involves intramolecular [3+2] cycloaddition of the C=N bond to the N-coordinated azide followed by internal rearrangement. The available evidence does not allow us to exclude the existence of other pathways to **4**, for example, via direct cyclisation of coordinated nitrile intermediates with azide anion [12a].



Scheme 1. Proposed pathways for the reactions of sodium azide with compound **1** [Mo–Mo=$Mo_2Cp_2(\mu\text{-}SMe)_3$].

The closest parallel to the work reported above would appear to be the synthesis by Lin et al. of the N-tetrazolate complex [$RuCp(PPh_3)_2\{N_4CC(Ph)CH_2CN\}$] [13]. This synthesis starts from a ruthenium cyclopropenyl complex and is only successful if one substituent of the cyclopropenyl ligand is a CN group. It uses Me_3SiN_3 instead of NaN_3 so that a hydrolysis step is required to generate azide. These differences preclude formation of the tetrazolate rings in **4** by the pathway suggested by Lin which goes successively through vinylidene and N-coordinated nitrile intermediates. Moreover, in our case removal of the alkyl hydrogen atom in **B** requires a specific step.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 189486 for complex **4a**. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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