A Bridging Side-on Allenylidene Dimolybdenum Complex without Carbonyl Stabilization

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Summary: The bis(nitrile) complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2](BF_4)$ **(1)** *reacts with* $HC{\equiv}CCPh_2(OH)$ *to give the* μ*-alkyne product* $[Mo_2Cp_2(\mu\text{-}SMe)_3\{HC{\equiv}CCPh_2(OH)\}](BF_4)$ **(2)**. *Sequential treatment with triethylamine and tetrafluoroboric acid converts* **2** *almost quantitatively, via the* μ*-alkynyl derivative* **3**, *into* $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}C{=}CPh_2)](BF_4)$ **(4)**, *the first example of a dinuclear* $\mu\text{-}\eta^1{:}\eta^2$*-allenylidene species without carbonyl ligands.*

Introduction

Recent interest[1] in allenylidene complexes arises from their importance in several developing areas of organometallic chemistry. (i) They are involved in the growth of carbon chains at metal surfaces.[1b] (ii) Their unsaturated carbon chains are possible precursors of molecular wires or polymers which have novel optical and electronic properties.[1c,2] (iii) They can catalyze synthetically useful organic reactions: for example, nucleophilic substitution of propargylic alcohols[3] and alkene metathesis.[4] The vast majority of known allenylidene complexes are mononuclear.[1] General methods of synthesis for binuclear or polynuclear derivatives are unavailable, and consequently, there have been only a few reports of such complexes.[5,6] Two well-established bridging modes have been found for allenylidenes in binuclear complexes, the $\mu\text{-}\eta^1{:}\eta^1$ (2e) (end-on)[5a,c,e,g−i] and $\mu\text{-}\eta^1{:}\eta^2$ (4e) (side-on)[5b,d,f] forms; however, there are also examples of dinuclear complexes containing nonbridging allenylidene ligands (2e).[3a,7] All known dinuclear and polynuclear complexes containing bridging allenylidene ligands also contain carbonyl ligands;[5,6] the only possible exception is $[\{Cp_2ZrEt\}_2(\mu\text{-}C{=}C{=}CMe_2)]$, where one Zr atom appears to interact with all three chain carbon atoms.[5k] Accordingly, in an attempt to synthesize μ-allenylidene complexes which do not owe their stability to the presence of carbonyl ligands, we have reacted the bis(isonitrile) compound $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2](BF_4)$ (**1**)[8] with propargylic alcohols, followed by sequential treatment with triethylamine and tetrafluoroboric acid. We now report that

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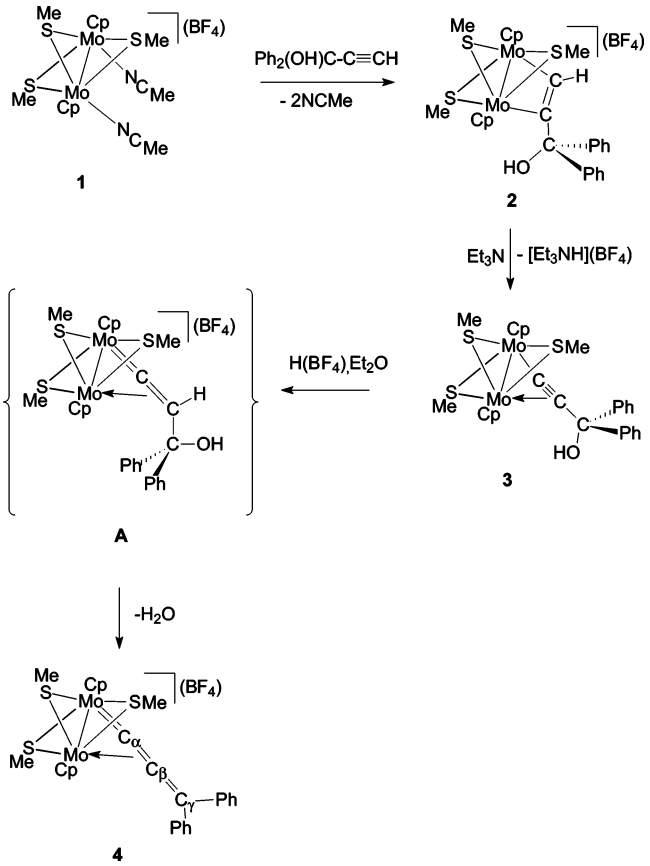
Scheme 1



the ultimate product of these reactions contains the desired C_3 ligand bridging two molybdenum atoms in a μ-η^1:η^2 (4e) manner.

Results and Discussion

Treatment of **1** with 1 equiv of $HC{\equiv}CCPh_2(OH)$ in CH_2Cl_2 gave $[Mo_2Cp_2(\mu\text{-}SMe)_3\{HC_2CPh_2(OH)\}](BF_4)$ (**2**) as a brownish green solid in 84% yield (Scheme 1). **2** is formulated as a dimolybdenum complex with an alkyne ligand bonded in a parallel μ-η^1:η^1 manner, since its spectra show obvious parallels with those of the related species $[Mo_2Cp_2(\mu\text{-}SPr^i)_2(\mu\text{-}S)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}C_2Ph_2)]$ and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HC_2CO_2Me)](BF_4)$, whose molecular structures have been confirmed by X-ray analysis.[9,10] In particular, the low-field ^{13}C chemical shift of the alkyne carbon atoms (δ 243.4) is in the range (δ 272−213)[9,10a,11] observed for other dinuclear complexes of group 6 metals, in which the alkyne group lies parallel to the metal−metal bond. This chemical shift differs strongly from the values (δ 87−62) reported for related compounds where the alkyne bridges two metals in the perpendicular μ-η^2:η^2 (4e) mode.[12]

Complex **2** was readily deprotonated in the presence of triethylamine to give a green solution from which the neutral acetylide derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CCPh_2(OH)\}]$ (**3**) was isolated in moderate yield (Scheme 1). The presence of the alkynyl ligand in **3** was established from both the $^{13}C\{^1H\}$ NMR spectrum and the $^1H-^{13}C$ experiment, which indicate the presence of only one resonance corresponding to the acetylenic carbon atoms[13] at 120.6 ppm and a singlet at 77.4 ppm due to the $CPh_2(OH)$ carbon atom. ^1H NMR spectra of **2** and **3** show only one Cp signal, which indicates that both complexes are fluxional at room temperature. Addition of HBF_4 to a solution of **3** in dichloromethane afforded exclusively the μ-allenylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2{=}C{=}C{=}CPh_2)](BF_4)$ (**4**) (Scheme 1). Mechanistically, the allenylidene-bridged derivative **4** most probably results from spontaneous dehydration of the μ-η^1:η^2−hydroxyvinylidene intermediate **A** (Scheme 1), generated by electrophilic attack of the proton of HBF_4 at the C_β carbon atom of the alkynyl complex **3**. The ^1H NMR spectrum of **4** shows a single cyclopentadienyl resonance at δ 6.00, which is integrated as 10 hydrogens. This is clearly inconsistent with the solid-state structure established for this complex (see below) and suggests that the molecule is fluxional in solution at room temperature. This is in accord with the observed line broadening of the Cp resonance when a dichloromethane-d_2 solution of **4** is cooled from 298 to 174 K. The $^{13}C\{^1H\}$ NMR spectrum contains a resonance at low field (δ 302.0) assignable to a carbenoid carbon atom (C_α). This low-field chemical shift is indicative of an asymmetric side-on coordination mode of the allenylidene group bridging a bimetallic core ([M]−[M]), for which a $^{13}C_\alpha$ chemical shift range of 302−282 ppm has been observed in known μ-allenylidene (side-on) dinuclear derivatives,[5b,d,f] and it is in contrast with the values of 206.5−173 ppm reported for related end-on species.[5a,c,e] In short, these spectroscopic data suggest that **4** has a highly unsymmetrical structure in solution. Single-crystal X-ray analysis confirms that the cation of **4** displays the unsymmetrical side-on coordination of the allenylidene group (Figure 1), bridging the metal−metal bond as a four-electron donor. However, a typical disorder of the μ-SMe groups (occupancy of minor sites 0.076(5)) affects the accuracy of the results. The length of the Mo−Mo single bond in **4** (2.659(9) Å) is close to the average value for $[Mo_2^{III}(\mu\text{-}SR)_3]$ complexes (2.644 Å), and the μ-Mo−S distances are also unexceptional.[14] The short Mo2−C4 distance (1.88(1) Å) formally represents a double bond; comparable distances are found in related neutral side-on allenylidene derivatives, such as $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C{=}CMe_2)]$ (1.912(3) Å)[5f] and $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C{=}C_6H_{10})]$ (1.90(1) Å),[5d] formally Mo(I) species, and in the cationic vinylidene derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2{=}C{=}CPh_2)](BF_4)$ (1.894(5) Å).[10a] In comparison to μ-η^1:η^1 (2e) allenylidene ligands, which are linear, the C_3Ph_2 fragment in **4** is kinked, with C4−C5−C6 = 144.0(1)°. The $C_\alpha-C_\beta$ and $C_\beta-C_\gamma$ distances of 1.31(2) and 1.36(1) Å are comparable to those observed in other side-on allenylidene complexes: i.e., 1.35(1) and 1.33(1) Å in $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C{=}C_6H_{10})]$[5d] and 1.336(3) and 1.348(4) Å in $[Mo_2Cp_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}C{=}CMe_2)]$.[5f]

In conclusion, the formation of the dinuclear μ-allenylidene complex **4** involves the four steps shown in Scheme 1. A similar

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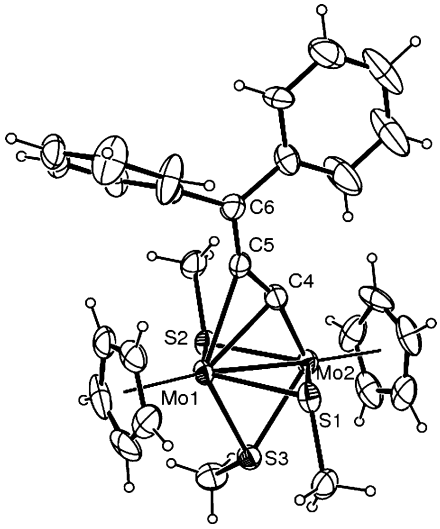

Figure 1. View of the $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}(C{=}C{=}CPh_2)]^+$ cation in crystals of **4**·CH_2Cl_2. Each S atom is disordered over two sites; only the major sites with occupancy 0.924(5) are shown here. Ellipsoids at the 20% probability level are shown, except for hydrogen atoms, which are represented by spheres of arbitrary radius. Selected distances (Å) and angles (deg): Mo1−Mo2, 2.659(9); Mo1−C4, 2.27(1); Mo1−C5, 2.44(1); Mo1−S1, 2.468(3); Mo1−S2, 2.482(3); Mo1−S3, 2.456(3); Mo2−C4, 1.88(1); Mo2−S1, 2.480(3); Mo2−S2, 2.497(3); Mo2−S3, 2.439(3); C4−C5, 1.31(2); C5−C6, 1.36(1); C6−C31, 1.51(1); C6−C41, 1.50(1); Mo1−C4−Mo2, 79.0 (4); C5−C4−Mo2, 160.1(9); C5−C4−Mo1, 81.3(7); C6−C5−C4, 144.0(1); C6−C5−Mo1, 149.3(8); C4−C5−Mo1, 66.6(7); C31−C6−C5, 121.9(9); C31−C6−C41, 118.2(9); C41−C6−C5, 119.8(9).

four-stage pathway was previously proposed by Selegue[15] for mononuclear transition-metal derivatives. Remarkable features of this work are that two of the three intermediates involved in the formation of **4** have been isolated and that, finally, a non-carbonyl μ-allenylidene dinuclear complex has been prepared and structurally characterized. Further experiments are now in progress: they extend the scope of the reactivity of these side-on allenylidene species and should give a better understanding of the factors which govern their behavior.

Experimental Section

General Procedures. All reactions were routinely carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from the appropriate drying agents. Literature methods were used for the synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_3(NCCH_3)_2](BF_4)$.[8] Other reagents were purchased from the usual commercial suppliers and used as received. Infrared spectra were recorded on a Nicolet-Nexus FT IR spectrophotometer from KBr pellets. Chemical analyses were performed by the Service de Microanalyse ICSN-CNRS, Gif sur Yvette, France. The NMR spectra (^1H, ^{13}C) were recorded at room temperature in CD_2Cl_2, $CDCl_3$, or C_6D_6 solution with a Bruker AMX 400 spectrometer and were referenced to $SiMe_4$. $^1H-^{13}C$ experiments were carried out on a Bruker DRX 500 spectrometer.

Synthesis of 2. A solution of complex **1** (200 mg, 0.32 mmol) in CH_2Cl_2 (20 mL) was stirred with 1 equiv of $HC{\equiv}CCPh_2(OH)$ (66 mg) for 50 min at room temperature. The solution turned from red to green. It was then concentrated, and 30 mL of diethyl ether was added. A brownish green solid precipitated and was collected by filtration and then washed with pentane (2 × 15 mL), giving an overall yield of 201 mg (84%) of **2**. IR (KBr, cm^{-1}): ν(OH) 3402 (vs), ν(C═C) 1635 (m). ^1H NMR (CD_2Cl_2, 25 °C): δ 12.52 (s, 1H, RCC*H*), 6.90−7.28 (m, 10H, $C(C_6H_5)_2$), 6.42 (s, 10H, C_5H_5), 3.21 (s, 1H, O*H*), 2,04, 2.02, and 1.99 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 243.4 (HC═*C*), 136.6 (*C* ipso Ph), 130.2−127.5 (C_6H_5), 106.7 and 98.3 (C_5H_5), 78.2 (*C*OH). 30.0 and 15.4 (SCH_3). Anal. Calcd for $C_{28}H_{31}BF_4Mo_2OS_3$: C, 44.34; H, 4.11. Found: C, 43.95; H, 4.31.

Reaction of 2 with Et_3N: Synthesis of 3. To a dark green solution of **2** (201 mg, 0.26 mmol) in CH_2Cl_2 (20 mL) was added an excess of triethylamine (2 equiv, 74 μL). The solution turned readily to pale green. After the mixture was stirred for a few minutes at ambient temperature, the solvent was evaporated and **3** was extracted with diethyl ether (2 × 15 mL). The solvent was then removed in vacuo from the pooled extracts. When the residue was washed with cold pentane, **3** was obtained as a green powder (84 mg, 47% yield). IR (KBr, cm^{-1}): ν(OH) 3412 (vs, br), ν(C≡C) 1959 (m). ^1H NMR ($CDCl_3$, 25 °C): δ 7.82−6.98 (m, 10H, $C(C_6H_5)_2$), 5.16 (s, 10H, C_5H_5), 2.57 (sbr, 1H, O*H*), 1.64, 1.61, and 1.49 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 147.2 (*C* ipso Ph), 130.1−126.8 (C_6H_5), 120.6 (C≡*C*CPh_2), 90.9 (C_5H_5), 77.4 (*C*(OH)Ph_2), 17.0, 11.8, and 10.9 (SCH_3). Anal. Calcd for $C_{28}H_{30}Mo_2OS_3$: C, 50.15; H, 4.51. Found: C, 50.21; H, 4.50.

Synthesis of 4. One equivalent of $H[BF_4]{\cdot}Et_2O$ in diethyl ether (5 mL) was added with stirring to a solution of **3** (84 mg, 0.125 mmol) in dichloromethane (10 mL) at room temperature. A purple solid readily precipitated from the solution and was collected by filtration and washed with pentane (2 × 15 mL). Compound **4** was obtained as a purple powder (78 mg, 75.5% yield). Crystals of **4**, suitable for X-ray analysis, were formed by crystallization at room temperature from a CH_2Cl_2 solution layered with diethyl ether. IR (KBr, cm^{-1}): ν(C═C═C) 1653 (m). ^1H NMR (CD_2Cl_2, 25 °C): δ 7.48−7.24 (m, 10H, $C(C_6H_5)_2$), 6.00 (s, 10H, C_5H_5), 2.01, 1.78, and 1.46 (s, 3H, SCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 302.0 (Mo_2C═C═CPh_2), 170.2 (Mo_2C═*C*═CPh_2), 140.2, 130.3, 130.2, and 129.1 (═C(C_6H_5)$_2$), 135.7 (Mo_2C═C═*C*Ph_2), 98.3 (C_5H_5), 25.6, 13.1, and 9.3 (SCH_3). Anal. Calcd for $C_{28}H_{29}BF_4Mo_2S_3{\cdot}CH_2Cl_2$: C, 42.20; H, 3.79. Found: C, 42.28; H, 3.92.

Crystallographic Data. X-ray crystal data for **4**·CH_2Cl_2: $C_{29}H_{31}BCl_2F_4Mo_2S_3$, fw = 825.31, monoclinic, space group $P2_1/c$, a = 10.4870(7) Å, b = 17.028(1_2) Å, c = 19.060(1_6) Å, β = 105.853(8)°, V = 3274.1(4) Å^3, T = 293 K, Z = 4, d(calcd) = 1.674 g/cm^3. 4888 unique, absorption-corrected intensities with θ(Mo Kα) < 25.0°. $R(F)$ = 0.079 for 3201 reflections with $I > 2\sigma(I)$, and $R_w(F^2$, all data) = 0.200 after refinement of 345 parameters. $|\Delta\rho|$ < 0.59 e Å^{-3}.

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Supporting Information Available: For **4**, tables giving details of structure determination, non-hydrogen atomic positional parameters, all bond distances and angles, anisotropic parameters and hydrogen atomic coordinates; crystallographic data are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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