Journal of Organometallic Chemistry 561 (1998) 49–56

Photolysis of $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}RC{\equiv}CR')$ in frozen Nujol matrices

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Received 20 October 1997; received in revised form 2 January 1998

Abstract

A series of compounds, $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-acetylene})$, where acetylene = 3-hexyne, diphenylacetylene, phenylacetylene and 1-phenylpropyne, was prepared and characterized by IR, ^1H- and ^{13}C-NMR spectroscopies and MS. Photolysis of these compounds was carried out in frozen Nujol at 77 K. IR spectra established the presence of two isomeric carbonyl-loss species, $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_2(\mu\text{-}\eta^1,\eta^2\text{-}CO)(\mu\text{-}\eta^{2:2}\text{-acetylene})$, **A**, and $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(\mu\text{-}CO)_3(\mu\text{-}\eta^{2:2}\text{-acetylene})$, **B**. **A** is formed by photolysis into low energy electronic transitions associated with the tetrahedrane core of the parent molecule, while **B** is formed by either photolysis into electronic bands associated with **A**, or photolysis into the high energy charge-transfer bands of the parent molecule. These photointermediates are likely to be involved in the formation of 'fly-over' compounds, resulting from thermally or photochemically induced multiple substitution of acetylenes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Molybdenum; Carbonyls; Cyclopentadienyls; Photochemistry; Matrices

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1. Introduction

Thermolysis or photolysis of the group VI bimetallic compounds $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ forms the triply-bonded species, $(\eta^5\text{-}C_5H_5)_2M_2(\mu\text{-}CO)_4$. For molybdenum, photolysis has been shown to proceed via photochemical loss of carbon monoxide to form $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^1,\eta^2\text{-}CO)$, which undergoes thermal loss of carbon monoxide to give $(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}CO)_4$ [1]. Subsequent reaction of these unsaturated species with acetylenes gives the tetrahedrane compounds, $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}RC{\equiv}CR)$ [2]. Amer and Pöe [3] established that the thermal reaction of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_6$ and acetylenes proceeds through carbon monoxide loss and not via radical processes.

Knox et al. [4] found that reaction of the tetrahedrane compounds with excess acetylene in refluxing heptane or octane resulted in sequential addition and linking of the acetylenes to yield products with up to four acetylene units coupled into a chain. These multiple acetylene-substituted products have been given the general name of 'fly-over' compounds. It was suggested that acetylene might add to $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}RC{\equiv}CR)$ by either a concerted addition to a M–acetylene bond, or by loss of carbon monoxide to yield an unsaturated intermediate that might subsequently react with acetylene. Somewhat later work by Green et al. [5] on indenyl molybdenum compounds, $(\eta^5\text{-}C_9H_7)_2Mo_2(CO)_4$, yielded the expected tetrahedrane derivatives, and also a series of 'fly-over' compounds. A complex reaction sequence involving dihapto-acetylene units and η^5 to η^3 indenyl shifts was proposed to account for the formation of the 'fly-over' species.

Recently, Kreiter et al. [6] have demonstrated that photolysis of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}HC{\equiv}CH)$ in

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PII S0022-328X(98)00512-9

the presence of excess acetylene yielded (η^5-C_5H_5)$_2$$M_2(CO)_2$($\mu$-$\eta^{1:3:3:1}$-$C_6H_6$), where M = Mo or W, and (η^5-C_5H_5)$_2$$Mo_2(CO)$($\mu$-$\eta^{1:4:1}$-$C_4H_4$). These workers proposed the reaction sequence in which initial photolysis of (η^5-C_5H_5)$_2$$M_2(CO)_4$($\mu$-$\eta^{2:2}$-HC≡CH) results in loss of carbon monoxide to form a coordinatively unsaturated intermediate that adds acetylene. Subsequent photochemical steps result in loss of carbon monoxide and either rearrangement to give (η^5-C_5H_5)$_2$$M_2(CO)$($\mu$-$\eta^{1:4:1}$-$C_4H_4$), or addition of a third acetylene to yield (η^5-C_5H_5)$_2$$M_2(CO)_2$($\mu$-$\eta^{1:3:3:1}$-$C_6H_6$). Clearly, such a sequence could also account for the thermal formation of the 'fly-over' compounds.

We have been examining the photochemistry of bimetallic compounds in both gas and frozen Nujol matrices and recognized that matrix photolysis of tetrahedrane compounds offered a simple way of establishing the identity of the photointermediates in these reactions. In this paper we present the synthesis and Nujol glass matrix photolysis of a series of tetrahedrane compounds and demonstrate a facile photochemical transformation between two isomeric forms of the carbonyl-loss photointermediate. These results are discussed in the light of the growing literature on photointermediates of bimetallic compounds.

2. Synthesis and characterization of (η^5-$C_5H_4C_4H_9$)$_2$Mo(CO)$_4$(μ-$\eta^{2:2}$-R–C≡CR′)

As noted in Section 1, tetrahedrane acetylene compounds may be prepared by reaction of the triply-bonded derivatives, (η^5-C_5H_5)$_2$$M_2$($\mu$-CO)$_4$, with acetylenes. For the current photolysis study, it was recognized that it was crucial to have tetrahedrane derivatives that would be soluble in Nujol at concentrations sufficient to obtain clear IR spectra. Preliminary experiments established that tetrahedrane compounds containing the unsubstituted cyclopentadienyl ligand were functionally insoluble in Nujol. To overcome this limitation (η^5-$C_5H_4C_4H_9$)$_2$$Mo_2(CO)_6$, **1**, was prepared as described in the literature [7]. Reaction of **1** with an acetylene in refluxing xylene yielded the desired tetrahedrane derivatives. By this route a series of compounds, (η^5-$C_5H_4C_4H_9$)$_2$$Mo_2(CO)_4$($\mu$-$\eta^{2:2}$-acetylene), where acetylene = 3-hexyne (**2**), diphenylacetylene (**3**), phenylacetylene (**4**), and 1-phenylpropyne (**5**), was prepared. IR spectra recorded during the reaction established the presence of (η^5-$C_5H_4C_4H_9$)$_2$$Mo_2(CO)_4$.

All of the tetrahedrane derivatives were isolated as either amorphous solids or as oils. As anticipated, these compounds had excellent solubility in Nujol. Unfortunately, this very property also made it difficult to remove all of the petroleum ether from the compounds, thus elemental analyses were poor. Residual traces of petroleum ether were observed in the NMR spectra of these samples. Further, in the case of **2**, a trace of **1** remained in the sample, even after careful chromatographic purification.

Fast atom bombardment (FAB) MS was carried out on compounds **2**–**5**, with molecular ions being observed in all cases. Although no fragment associated with loss of only a single carbon monoxide ligand was observed, loss of two carbon monoxide ligands was found to be the dominant fragmentation process.

^{1}H- and ^{13}C-NMR spectra of the tetrahedrane compounds were consistent with those of analogous nonsubstituted cyclopentadienyl compounds. Carbonyl resonances were observed for compounds **2**–**4**, but not for **5**. Compounds **2** and **3** were found to have a single carbonyl resonance, while compound **4** had two carbonyl resonances, consistent with the presence of an asymmetric acetylene in **4**. In all cases, carbonyl groups shuttle between terminal and semibridging carbonyl positions at a rate that must be fast on the NMR time scale.

3. Photochemical studies in frozen Nujol at 77 K

We have previously reported the photolysis of (η^5-C_5H_5)$_2$$Mo_2(CO)_6$ in frozen gas matrices at 12 K [8]. Under these conditions, photolysis results in loss of carbon monoxide to yield (η^5-C_5H_5)$_2$$Mo_2(CO)_2$($\mu$-CO)$_2$($\mu$-$\eta^1$,$\eta^2$-CO), Fig. 1, having terminal, semibridging, and four-electron bridging carbonyl groups. This species has also been observed in flash photolysis studies [1]. For comparison we examined the photolysis of (η^5-$C_5H_4C_4H_9$)$_2$$Mo_2(CO)_6$ in frozen Nujol at 77 K. In frozen Nujol, **1** was found to have three bands at 1956, 1913 and 1906 cm^{-1}, as shown in Fig. 2(a). Photolysis resulted in a decrease in the bands of **1** and growth of new bands at 2132 (w), 1976 (m), 1933 (s), 1892 (w), 1861 (m) and 1665 (m) cm^{-1}, Fig. 2(b). Bands at 2132 cm^{-1} are associated with 'free' carbon monoxide in Nujol matrices. The pattern and positions of the remaining bands associated with the photolysis product are quite similar to those of (η^5-C_5H_5)$_2$$Mo_2(CO)_2$($\mu$-CO)$_2$($\mu$-$\eta^1$,$\eta^2$-CO) in frozen methane, Table 1, and indicate that the presence of butyl substituents on the cyclopentadienyl ring do not alter the photochemical behavior of the compound.

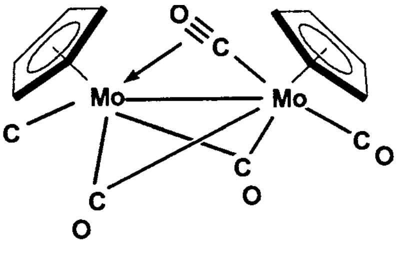


Fig. 1. Proposed structure of (η^5-C_5H_5)$_2$$Mo_2(CO)_2$($\mu$-CO)$_2$($\mu$-$\eta^1$,$\eta^2$-CO).

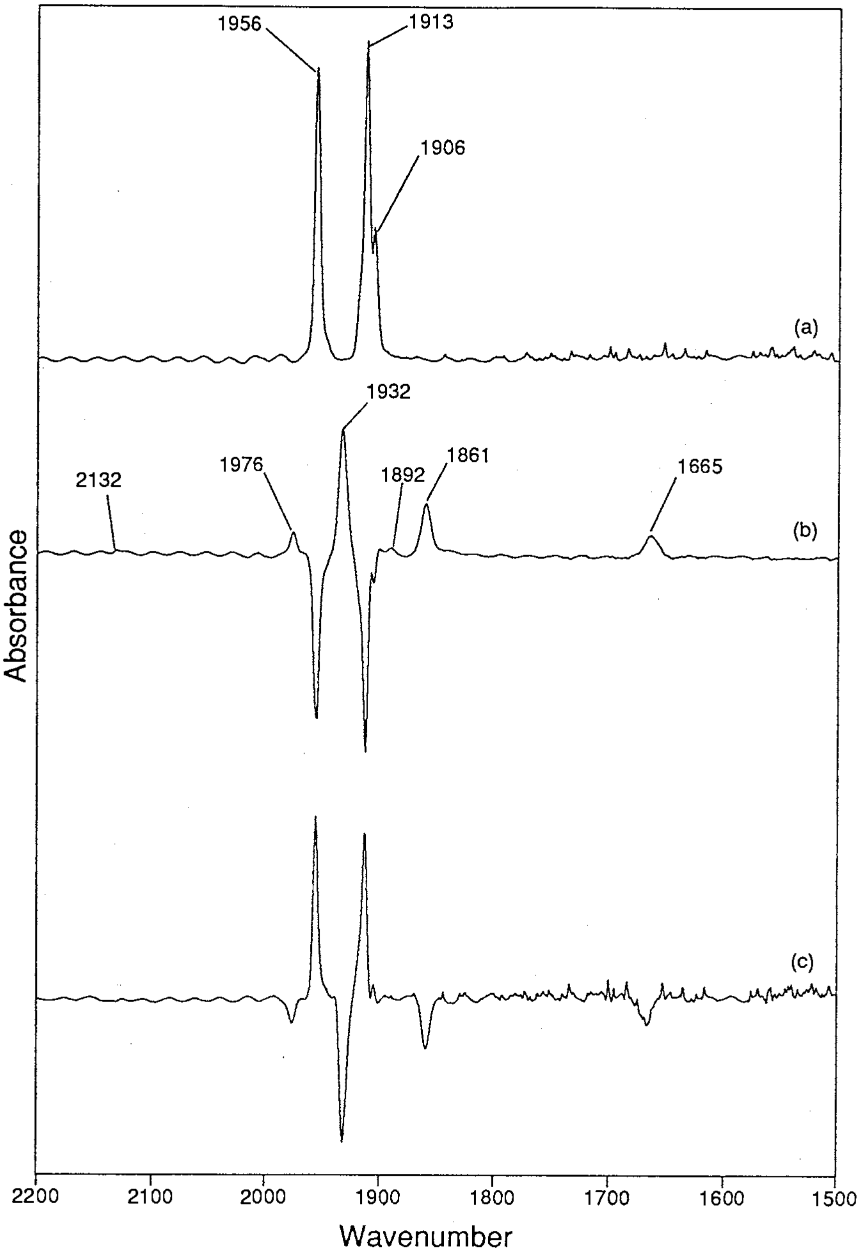


Fig. 2. (a) IR spectrum of $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_6$ in Nujol glass at ca. 77 K. (b) 30 min photolysis (400 ± 70 nm)-starting material. (c) 15 min anneal to ca. 173 K-30 min photolysis.

In Nujol at 77 K, the IR spectra of compounds **3** and **5** in the carbonyl region contain three bands, while those of **2** and **4** contain four. In each case, one of these bands (1833–1843 cm^{-1}) may be attributed to a semibridging carbonyl, while the remaining bands are associated with terminal carbonyl stretching modes. Molecular structures of analogous unsubstituted cyclopentadienyl compounds establish that these molecules are asymmetric in the solid-state with three terminal carbonyl groups and one semibridging carbonyl group [9]. Symmetry arguments would predict a total of four carbonyl stretching bands for these compounds, thus it is likely that two central bands overlap in compounds **3** and **5**.

Electronic spectra of compounds **2**–**5** contain two distinct features at ca. 535 and 360 nm, and an ill-defined shoulder at ca. 460 nm. By comparison, the electronic spectrum of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}HC{\equiv}CC_6H_5)$ has been reported to have bands at 543 and 362 nm in isooctane at room temperature ([2]c). It is likely that low temperature sharpening of the spectra permitted the shoulders at ca. 460 nm to be observed for compounds **2**–**5**. The bands at 535 and 460 nm may be associated with the tetrahedrane core of the molecule, while the more intense absorbance at 360 nm is most likely a metal-to-ligand charge-transfer band. Hoffmann and coworkers have described the bonding in perpendicular and parallel acetylene complexes and find that the bonding within the tetrahedrane core is delocalized [10]. At present, theory does not provide guidance as to the actual nature of the excited states in these compounds.

The IR spectrum of **2** is shown in Fig. 3(a). Bands at 1989, 1914, 1905 and 1833 cm^{-1} are attributable to carbonyl groups of **2**. The small band at 1956 cm^{-1} is due to a trace of **1**, which was not removed by chromatography. Photolysis of **2** at 550 nm (± 70 nm) for 30 min results in the loss of IR bands associated with **2** and the growth of new bands at 2132 (w), 1935 (m), 1917 (s), 1794 (w) and 1678 (s) cm^{-1}, Fig. 3(b). The photoproduct of **1** makes a small contribution to the product band at 1935 cm^{-1} in Fig. 3(b). Electronic spectra recorded on this sample revealed that the bands associated with **2** had been bleached, while new bands were observed at 550 and 450 nm.

Continued photolysis of this sample at 450 nm (± 70 nm) for 30 min resulted in decreases of those bands associated with **2** and those at 1935, 1917 and 1678 cm^{-1}, while the bands at 2132 and 1794 cm^{-1} continued to grow, Fig. 3(c). As the band at 1794 cm^{-1} increased in intensity, it became apparent that it was asymmetric with a shoulder at ca. 1760 cm^{-1}. A new band was found in the electronic spectrum at 490 nm.

Photolysis of a fresh sample of **2** for 60 min at 360 nm (± 10 nm) resulted in a decrease in the parent bands, and appearance of the same bands as found at 550 nm, except that the bands at 1794 and 1760 cm^{-1} were substantially more intense than those at 1935, 1917 and 1678 cm^{-1}.

Annealing this sample to 157 K resulted in bands at 2132, 1935, 1917 and 1678 decreasing, while those of the parent species and bands at 1794 and 1760 increased in intensity. Finally, annealing the sample to 177 K resulted in bands at 2132, 1794 and 1760 cm^{-1} decreasing in intensity, while those of the parent species grew.

Table 1
Carbonyl stretching frequencies of $(\eta^5\text{-}C_5H_4R)_2Mo_2(CO)_6$ and their photoproducts in cm^{-1}

Compound	L–C_5H_5 [a]	L=$C_5H_4C_4H_9$ [b]
$L_2Mo_2(CO)_6$	1963 1919 1912	1955 1913 1906
$L_2Mo_2(CO)_5$	1982 1940 1886 1865 1667	1975 1933 1892 1861 1664

[a] CH_4 matrix, 12 K [8]
[b] Nujol glass matrix, 77 K (this work).

Photolysis of compounds **3**–**5** resulted in very similar observations. The IR spectral data for all compounds and photoproducts are summarized in Table 2. Electronic spectral data for compounds **2**–**5** are presented in Table 3. Annealing samples of **3**–**5** after photolysis resulted in the appearance of small, but reproducible, bands ca. 2182 and 2040 cm^{-1}. These bands appeared only in those compounds with phenyl groups on the acetylene, ruling out the possibility of N_2 compounds that are sometimes observed to arise from nitrogen dissolved in the Nujol. Since absorbances in the range of 2182 cm^{-1} are typical for metal-hydrides, we tentatively propose that oxidative addition (*ortho* metallation) of a phenyl C–H bond into an electronically unsaturated molybdenum results in the formation of a species such as illustrated in Fig. 4. Oxidative addition of cyclopentadienyl C–H bonds by electronically unsaturated metals in bimetallic species have been observed by Riera and coworkers [11] and ourselves [12]. We are presently examining this photolysis on the preparative scale to clarify the identity of these new species.

In all cases, the photolysis of the parent tetrahedrane species results in loss of carbon monoxide to yield two photoproducts, **A** and **B**. Low energy photolysis into the absorption bands associated with the tetrahedrane core of the parent molecule yields **A**, having three absorption bands that may be assigned to two terminal carbonyl groups and a four-electron bridging carbonyl group. That the absorption band of the four-electron bridging carbonyl was not observed in the photolysis of **3** may only reflect the lower solubility of **3** in Nujol. Photolysis into the electronic absorption bands of **A** yields **B** with IR absorption bands between 1800 and 1750 cm^{-1}. **B** appears to be a photochemical rearrangement product of **A** having only bridging carbonyl groups. **B** may also be directly generated by photolysis into the charge-transfer bonds of the parent compounds, although it is not possible to preclude the possibility that **A** is still the intermediary in the high energy photolysis. These processes are summarized in Scheme 1.

The initial photointermediate in this sequence, **A**, is strikingly similar to the photoproducts of **1** and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$. In these cases, loss of a carbon monoxide ligand is compensated for by one of the remaining carbonyl groups serving as a four-electron donor. Such a species was originally suggested by Kreiter et al. as an intermediate in the addition of acetylene to the tetrahedrane species. Subsequent rearrangement of **A** yields **B**, with all bridging carbonyl groups. Similar geometries with bridging or semibridging carbonyl groups are known for the electron-deficient species: $(\eta^5\text{-}C_5H_5)_2M_2(\mu\text{-}CO)_4$, where M = Cr, Mo, and W [1], $(\eta^5\text{-}C_5H_5)_2M_2(\mu\text{-}CO)_3$, where M = Fe and Ru [13], $(\eta^5\text{-}$

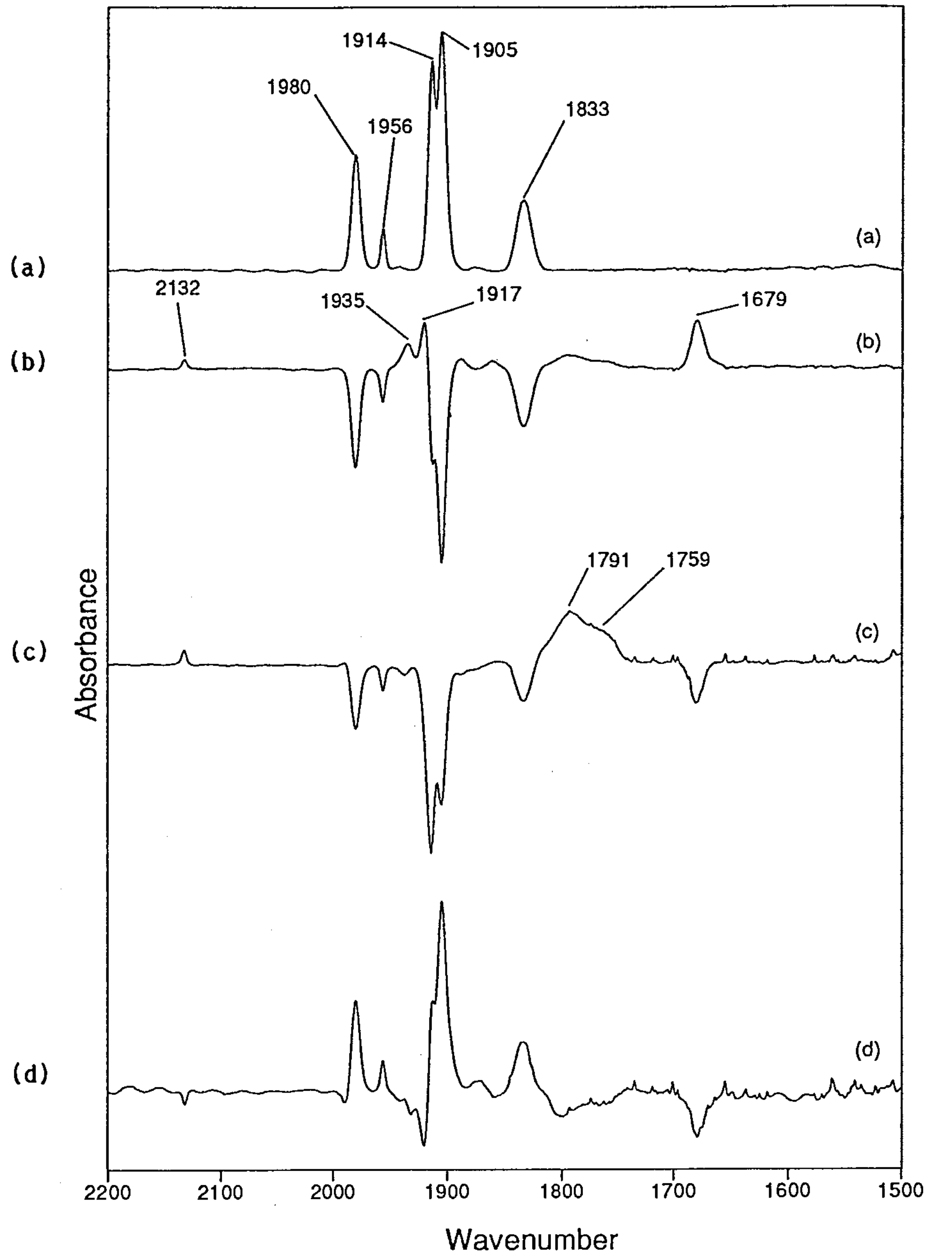


Fig. 3. (a) IR spectrum of (η^5-$C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu$-$\eta^{2:2}$-$C_2H_5$–C≡C–$C_2H_5$) in Nujol glass at ca. 77 K. (b) 30 min photolysis (550 ± 70 nm)-starting material. (c) 60 min photolysis (450 ± 70 nm)-30 min photolysis. (d) 15 min anneal to ca. 173 K-60 min photolysis. (Note: band at 1956 cm^{-1} is due to trace of **1**.

$C_5Me_5)_2Re_2(CO)_3$ [14], (η^5-$C_5H_5)_2M_2(\mu$-$CO)_2$, where M = Co and Rh [15], (η^5-$C_5H_5)_2Fe_2(\mu$-$CO)_2(\mu$-$CHCH_3$) [16] and the acetylenic species, (η^5-$C_5H_5)_2Ru_2(\mu$-CO)(μ-$\eta^{2:2}$-Ph–C≡C–Ph) [17].

Zhang and Brown reported a detailed examination of the flash photolysis of (η^5-$C_5H_5)_2Fe_2(CO)_4$ and have established the formation of two carbonyl loss species, the known (η^5-$C_5H_5)_2Fe_2(\mu$-$CO)_3$ and (η^5-$C_5H_5)_2Fe_2(\mu$-$CO)_2(\mu$-η^1,η^2-CO). It is proposed that the four-electron semibridging species converts to the triply-bridged species by a photochemical process [18]. This reaction appears to parallel the observation reported here of the photochemical conversion of (η^5-$C_5H_4C_4H_9)_2Mo_2(CO)_2(\mu$-$\eta^1,\eta^2$-CO)($\mu$-$\eta^{2:2}$-RC≡CR) into ($\eta^5$-$C_5H_4C_4H_9)_2Mo_2(CO)_3(\mu$-$\eta^{2:2}$-RC≡CR).

4. Experimental

All syntheses were performed under an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and distilled over a sodium–potassium alloy or calcium hydride under an atmosphere of nitrogen. Preparative chromatography was conducted

Table 2
Carbonyl stretching frequencies of the acetylene compounds in cm^{-1}

Compound[a]	Nujol at 77 K	Dichloromethane[b]	Petroleum ether[b]
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-EtC}\equiv\text{CEt})$ (**2**)	1980	1972	
	1914		
	1905	1903	
	1833	1821	
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-EtC}\equiv\text{CEt})$ (**2-A**)	1935		
	1917		
	1679		
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-EtC}\equiv\text{CEt})$ (**2-B**)	1791		
	1759		
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CPh})$ (**3**)	1984	1981	
	1926	1920	
	1843	1834	
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CPh})$ (**3-A**)	1943		
	1910		
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CPh})$ (**3-B**)	1823		
	1806		
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CCH}_3)$ (**4**)	1982	1978	
	1922		
	1914	1911	
	1838	1828	
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CCH}_3)$ (**4-A**)	1947		
	1897		
	1681		
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CCH}_3)$ (**4-B**)	1815		
	1797		
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CH})$ (**5**)	1988	1985	1990
	1925	1918	1929
	1842	1830	1848
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CH})$ (**5-A**)	1936		
	1899		
	1682		
$(BuCp)_2Mo_2(CO)_3(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CH})$ (**5-B**)	1806		

[a] $BuCp = (\eta^5\text{-}C_5H_4C_4H_9)$, $Et = CH_2CH_3$, $Ph = C_6H_5$.
[b] Room temperature.

using solvents flushed with nitrogen and neutral alumina from CAMAG.

^1H- and ^{13}C-NMR spectra were recorded at 300 and 75 MHz, respectively, using a Brüker NR-300 spectrometer or a Varian Gemini-300 spectrometer. IR spectra of solution samples were recorded using a Bio-Rad Qualimatic FT-IR. MS was carried out by Dr Gary Knerr using the FAB, electron impact and chemical ionization modes on a VG 7070-HS GC/MS.

Table 3
Electronic absorption bands of acetylene compounds in the Nujol matrix at ca. 77 K

Compound[a]	Absorbance maxima (nm)		
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-EtC}\equiv\text{CEt})$ (**2**)	360[b]	480[c]	535[c]
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CPh})$ (**3**)	352	466	540
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CCH}_3)$ (**4**)	353	460	539
$(BuCp)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-PhC}\equiv\text{CH})$ (**5**)	356	450	533

[a] $BuCp = (\eta^5\text{-}C_5H_4C_4H_9)$, $Et = CH_2CH_3$, $Ph = C_6H_5$.
[b] Metal-to-ligand charge-transfer.
[c] Tetrahedrane core.

1 was prepared by literature methods [7]. Acetylenes were purchased from Strem Chemical or Aldrich, and used as-received.

Photochemical studies were carried out in a cryostat designed by Dr Antony Rest of the University of Southampton. Experimental details on the use of the cryostat have been previously described [19]. Nujol

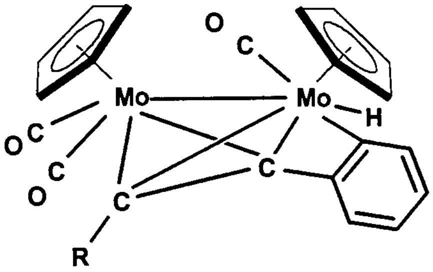
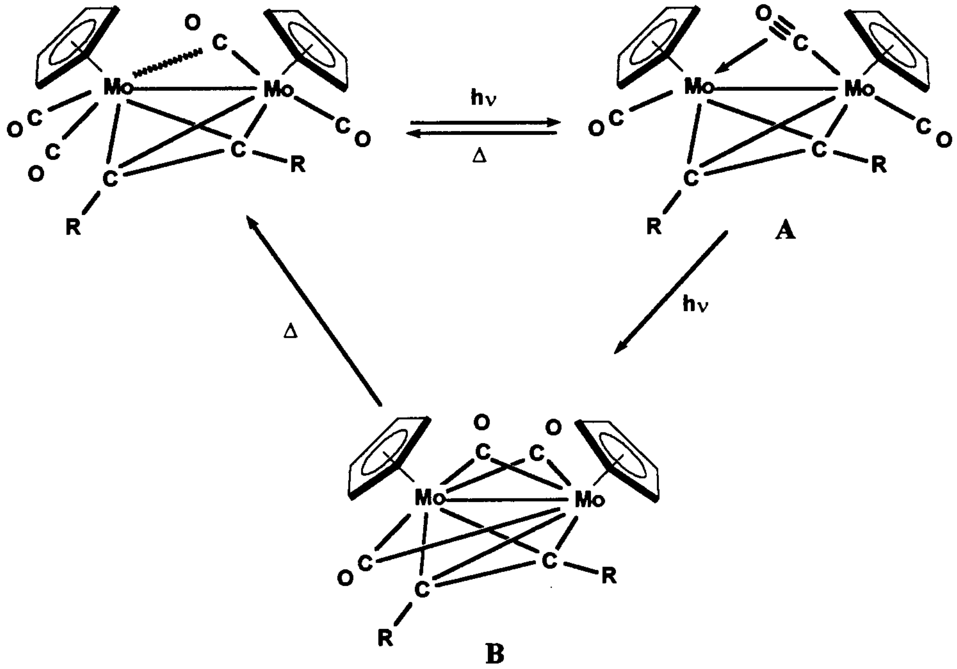


Fig. 4. Proposed structure of phenyl oxidative addition annealing product.



Scheme 1. Photolysis of tetrahedrane acetylene derivatives.

matrix isolation work was performed using a Bio-Rad FTS 15/80 FT-IR spectrometer. Spectra were collected using a liquid nitrogen-cooled mercury cadmium telluride (MCTB) detector. Spectra were recorded using 1024 scans and a resolution of 2 cm^{-1}. Each sample was allowed to sit for 20 min prior to recording spectra while the instrument and the sample compartment purged with dry air.

4.1. General procedures for the synthesis of tetrahedrane acetylene compounds

A Schlenk flask was evacuated and back-filled with nitrogen. Xylenes, 50 ml, and **1** (0.50g, 0.83 mmol) were added to the Schlenk flask under nitrogen. One equivalent of acetylene was added using a microliter syringe. The mixture was refluxed overnight while nitrogen was bubbled through the reaction mixture. After removal of solvent under reduced pressure, the reaction mixture was taken up in petroleum ether and chromatographed using petroleum ether as an eluant. In all cases, three bands were observed. An initial green band was observed, but decomposed on the column, followed by a light pink band that was determined to be unreacted starting material. Continued elution recovered a dark red band that was determined to be the desired product. Three of the four compounds were oils, and the fourth an amorphous solid. Extended periods under vacuum failed to remove all of the petroleum ether from these samples.

*4.1.1. $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}CH_3CH_2C{\equiv}CCH_2CH_3)$, **2***

Maroon amorphous solid. m.p. 46.7–47.0°C, 35.5% yield. IR (cm^{-1}, CH_2Cl_2): 1972, 1903 and 1821. ^{1}H-NMR (δ, $CDCl_3$): 5.02 (m, AA′BB′, 8H, Cp), 2.76 (q, $J_{C\text{–}H} = 7.30$ Hz, 4H, Et–CH_2), 2.28 (t, $J_{C\text{–}H} = 7.20$ Hz, 4H, Bu–CH_2), 1.44 (m, 4H, Bu–CH_2), 1.30 (m, 4H, Bu–CH_2), 0.976 (t, $J_{C\text{–}H} = 7.35$ Hz, 6H, Et–CH_3) and 0.849 (t, $J_{C\text{–}H} = 7.25$ Hz, 6H, Bu–CH_3). ^{13}C-NMR (δ, $CDCl_3$): 232 (CO), 112 (*ipso* Cp), 94 (Cp), 91 (acetylenic carbon), 90 (Cp), 88 (acetylenic carbon), 34 (Bu–CH_2), 30 (acetylenic–CH_2), 29 (Bu–CH_2), 23 (Bu–CH_2), 15.6 (acetylenic–CH_3) and 14 (Bu–CH_3). MS: 630 ($M^+ + 2$, 2%), 628 (M^+, 2%), 572 (M^+-2CO, 37%), 547 (M^+-RCCR, 18%), 544 (M^+-3CO, 23%), 512 (M^+-2CO-Bu, 100%), and 425 (M^+-BuCp–RCCR, 13%). Anal. calc. for $C_{28}H_{36}O_4Mo_2$: C, 53.51; H, 5.77. Found: C, 55.19; H, 6.41.

*4.1.2. $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}C_6H_5C{\equiv}CC_6H_6)$, **3***

Dark red oil. 24.8% yield. IR (cm^{-1}, CH_2Cl_2): 1981, 1920 and 1834. ^{1}H-NMR (δ, $CDCl_3$): 7.11 (m, 10H, Ph), 4.94 (m, AA′BB′, 8H, Cp), 2.32 (t, $J_{C\text{–}H} = 7.47$ Hz, 4H, CH_2), 1.46 (m, 4H, CH_2), 1.15 (m, 4H, CH_2) and 0.847 (t, $J_{C\text{–}H} = 7.03$ Hz, 6H, CH_3). ^{13}C-NMR (δ, $CDCl_3$): 231.6 (CO), 146 (*ipso* Ph), 129 (*o*-Ph), 128 (*m*-Ph), 125 (*p*-Ph), 113 (*ipso* Cp), 95 (Cp), 92 (Cp), 80 (acetylenic carbon), 34 (CH_2), 28 (CH_2), 22 (CH_2) and 14 (CH_3). MS: 726.5 ($M^+ + 2$, 10%), 724.5 (M^+, 11%), 668 (M^+-2CO, 100%), 641 (M^+-3CO, 27%), 612 (M^+-

2CO–Bu, 57%), 547 (M^+-RCCR, 5%), 518 (M^+-CO–RCCR, 10%), 489 (M^+-Bu–RCCR, 10%) and 423 (M^+-BuCp–RCCR, 27%). Anal. calc. for $C_{36}H_{36}O_4Mo_2$: C, 59.68; H, 5.00. Found: C, 61.10; H, 5.31.

4.1.3. $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}CH_3C\equiv CC_6H_6)$, **4**

Dark red oil. 31.6% yield. IR (cm^{-1}, CH_2Cl_2): 1978, 1911 and 1828. ^{1}H-NMR (δ, $CDCl_3$): 7.11 (m, 5H, Ph), 4.97 (m, AA′BB′, 8H, Cp), 2.60 (s, 3H, acetylenic CH_3), 2.24 (t, $J_{C–H} = 7.60$ Hz, 4H, CH_2), 1.38 (m, 4H, CH_2), 1.26 (m, 4H, CH_2), and 0.91 (t, $J_{C–H} = 7.20$ Hz, 6H, Bu–CH_3). ^{13}C-NMR (δ, $CDCl_3$): 231.8, 231.6 (CO), 146 (*ipso* Ph), 129 (*o*-Ph), 128 (*m*-Ph), 125 (*p*-Ph), 113 (*ipso* Cp), 94.4, 93.8, 91.1, 90.7 (Cp), 81.5, 80.7 (acetylenic carbons), 34 (CH_2), 28 (CH_2), 24 (CH_3, acetylenic), 22 (CH_2), and 14 (CH_3). MS: 663 (M^+, 15%), 607 (M^+-2CO, 100%), 579 (M^+-3CO, 11%), 550 (M^+-2CO–Bu, 72%), 547 (M^+-RCCR, 62%), 519 (M^+-CO–RCCR, 10%), 489 (M^+-Bu–RCCR, 8%), and 423 (M^+-BuCp–RCCR, 29%). Anal. calc. for $C_{31}H_{34}O_4Mo_2$: C, 56.21; H, 5.17. Found: C, 56.90; H, 5.22.

4.1.4. $(\eta^5\text{-}C_5H_4C_4H_9)_2Mo_2(CO)_4(\mu\text{-}\eta^{2:2}\text{-}HC\equiv CC_6H_6)$, **5**

Dark red oil. 20.8% yield. IR (cm^{-1}, CH_2Cl_2): 1985, 1918 and 1830. IR (cm^{-1}, petroleum ether): 1990, 1929, 1848. ^{1}H-NMR (δ, $CDCl_3$): 7.23 (m, 5H, Ph), 5.34 (s, 1H, acetylenic H), 5.16 (m, AA′BB′, 8H, Cp), 2.21 (t, $J_{C–H} = 7.25$ Hz, 4H, CH_2), 1.40 (m, 8H, CH_2CH_2), and 0.864 (t, $J_{C–H} = 7.05$ Hz, 6H, CH_3). ^{13}C-NMR (δ, $CDCl_3$): 153 (*ipso* Ph), 130 (*o*-Ph), 129 (*m*-Ph), 126 (*p*-Ph), 93 (Cp), 91 (Cp), 33 (CH_2), 28 (CH_2), 22 (CH_2) and 13 (CH_3). MS: 650 ($M^+ + 2$, 12%), 648 (M^+, 12%), 592 (M^+-2CO, 100%), 564 (M^+-3CO, 11%), 547 (M^+-RCCR, 10%), 535 (M^+-2CO–Bu, 59%), 489 (M^+-Bu–RCCR, 11%) and 425 (M^+-BuCp–RCCR, 35%).

Acknowledgements

We thank Research Corporation for a generous Research Opportunity Award for the purchase of an FT-IR spectrometer. Our thanks to Professor Dr Cornelius Kreiter for helpful discussions and Dr Antony Rest for the gift of the cryostat used in these studies.

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