

Journal of Organometallic Chemistry, 157 (1978) 41–50
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**SYNTHESIS AND X-RAY CRYSTALLOGRAPHIC STRUCTURAL
 DETERMINATION OF THE ACETYLENE COMPLEX**
 $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$

DAVID S. GINLEY, C. RANDOLPH BOCK, MARK S. WRIGHTON^{*,**},

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts
 02139 (U.S.A.)*

BEDA FISCHER, DONALD L. TIPTON and ROBERT BAU^{*,**}

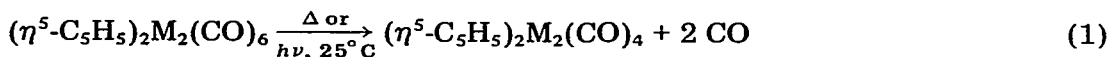
*Department of Chemistry, University of Southern California, Los Angeles, California 90007
 (U.S.A.)*

(Received September 21st, 1977)

Summary

Reaction of photogenerated $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$ with acetylene at 25°C yields a complex of the formula $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$. The crystal structure of the complex shows it to have a tetrahedrane-like W_2C_2 core. The C—C bond distance of the C_2H_2 unit is 1.33 Å which is close to that of ethylene, considerably longer than the 1.20 Å for acetylenes. The W—W distance is 2.987 Å which is ~0.25 Å shorter than the W—W distance in $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$ but longer than that expected for $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$. By analogy to the parent $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$ species, the near-UV absorption in $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ is assigned to a $\sigma_b \rightarrow \sigma^*$ transition. Owing to the shorter M—M bond in the C_2H_2 adducts, the $\sigma_b \rightarrow \sigma^*$ absorption is at higher energy than in the $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$ complexes.

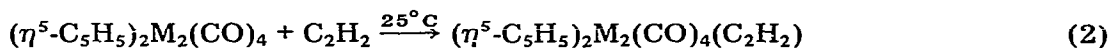
The chemistry indicated in reaction (1) was recently reported [1–3]. Subsequent reaction of the metal—metal triple bonded complex with C_2H_2 occurs according to reaction (2) [2,3]. Reaction (2) seems to represent the only example of the direct reaction of a triple metal—metal bonded complex with another



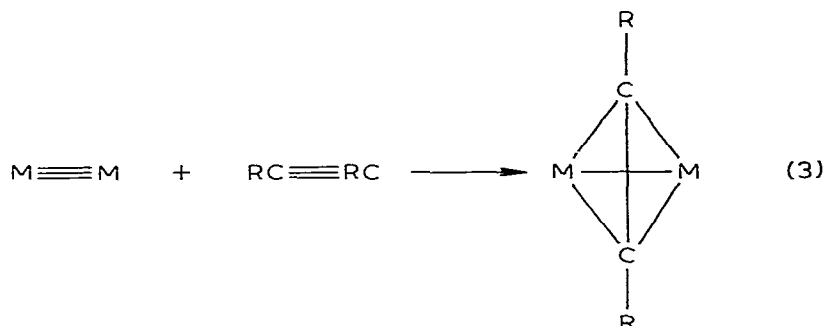
M = Mo, W

* Dreyfus Teacher-Scholar Grant Recipient, 1975–1980.

** NIH Research Career Development Awardee, 1975–1980.



triple bonded species. The reaction may be viewed as in reaction (3).



Owing to the potential importance of such reactions in building up clusters, and acetylene-containing clusters especially, we have undertaken an X-ray crystallographic structural determination of the acetylene adduct formed from the reaction of C_2H_2 and photogenerated $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$ [2]. Some structural features of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{R}_2)$ ($\text{R} = \text{C}_2\text{H}_5, \text{H}$) have already been reported [4].

Results and discussion

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$

Irradiation of an Ar-purged benzene solution of $\sim 10^{-2} M$ $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$ with near-UV light at 25°C leads to the decline of IR bands at 1958 and 1910 cm^{-1} and the concomitant growth of new bands at 1885 and 1930 cm^{-1} . The irradiation was carried out using a GE Blacklight with two 15 W lamps having a maximum output at 355 nm. Accompanying these changes is a general decline of the near-UV and UV-vis absorption spectrum associated with $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$. The original red-purple solution ultimately becomes yellow. The yellow solution contains the $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$ species. Its PMR, IR, and UV-vis properties are in accord with this formulation [1,2], and the synthesis and spectral properties accord well with those for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ [1-3] for which an X-ray crystallographic structural determination has been made [3].

Purging a benzene solution of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$ with C_2H_2 results in essentially immediate reaction as evidenced by the change of color from yellow to red-purple. Rotary evaporation of the solvent, chromatography on grade 1 alumina eluting with CH_2Cl_2 , and recrystallization from benzene/pentane yields a complex of the formula $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$. The C, H analysis is satisfactory: Found, C, 30.2; H, 2.1. Calcd., C, 30.2; H, 1.9%. Consistent with its formulation as a tetrahedrane-like species the PMR in CDCl_3 exhibits two singlets in a 5 : 1 ratio at 4.64 (C_5H_5) and 6.11 (C_2H_2) τ . The electronic spectrum in benzene at 298 K reveals maxima at 525 ($\epsilon = 900$) and 352 ($\epsilon = 6000$) nm, and the IR in the CO stretching region shows three peaks: 1990, 1922, and 1835 cm^{-1} (isooctane solvent). These spectral properties parallel those for the Mo analogue [3].

X-ray crystallographic structural determination of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$

The specimen, a rectangular parallelepiped with dimensions $0.35 \times 0.30 \times 0.20$ mm, was mounted on a glass fiber along the b axis. Preliminary precession photographs revealed the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 10.324(4)$, $b = 17.225(5)$, $c = 8.582(3)$, $\beta = 94.8(4)$, $Z = 4$, $V = 1528.4 \text{ \AA}^3$. The unit cell parameters were obtained from the setting angles of 15-well-centered, high angle reflections. Other relevant data are: Mol. wt. = 635.8, $\rho_{\text{obs}} = 2.78 \text{ g cm}^{-3}$ (obtained by flotation in aqueous ZnI_2), $\rho_{\text{calc}} = 2.81 \text{ g cm}^{-3}$, $\mu = 161 \text{ cm}^{-1}$ (for $\text{Mo-K}\alpha$ X-rays).

Data were collected in the $(\pm h, +k, +l)$ quadrant on a Syntex $P2_1$ diffractometer with graphite monochromator and $\text{Mo-K}\alpha$ X-rays by the $\theta/2\theta$ scan technique up to a 2θ limit of 45° . The scan speed varied between 4.0 and $29.8^\circ/\text{min}$ according to the intensity of the reflection; the scan range was defined as $\Delta 2\theta = 1.2^\circ$. Each reflection was scanned once with background counts taken at the beginning and end of each scan. As a check on the stability of the diffractometer and the crystal, the $(0, 6, 0)$, $(-6, 0, 0)$, and $(0, 0, 4)$ reflections were measured at fifty reflections intervals. No significant variation in the intensities was observed during the data collection. 3023 non-negative reflections (excluding check reflections) were collected, of which 2830 were unique. Of these, 498 were rejected as too weak. The remaining 2332 reflections were corrected for Lorentz and polarization effects. The standard deviation of each reflection was estimated from counting statistics. An empirical absorption correction was applied based on the variation of intensity of the $(0, 6, 0)$ reflection around the diffraction vector (ψ scan). Transmission factors (normalized to unity) varied between 0.59 and 3.14; this large variation is consistent with the large linear absorption coefficient of the compound. No significant dependence of absorption upon 2θ was found.

The structure was solved with conventional heavy atom methods; the coordinates of the W atoms were obtained from a Patterson map, and all other non-hydrogen atoms were located from difference Fourier maps. In the subsequent least-squares refinement, the thermal parameters of the tungsten atoms were refined anisotropically, while those of the carbon and oxygen atoms were refined isotropically. A final difference Fourier map showed some residual electron density on the vicinity of the cyclopentadiene rings, indicating considerable vibrational motion of the rings about the metal-ring axis. The final agreement factors are $R = 0.073$ and $R_w = 0.088$ *.

An ORTEP plot of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ is shown in Fig. 1, and the atomic positions, distances and angles are set out in Tables 1 and 2. The W—W bond is $2.987(1) \text{ \AA}$ long and is bridged by the acetylene group in a nearly perpendicular fashion (the angle between the W—W bond and the C—C bond, looking down the center of both bonds, is 87°). The bond distances from the tungsten atoms to the acetylenic carbon atoms are identical within 3σ and their average is $2.16(2)$

* The table of structure factors has been deposited as NAPS Document No. 03313 (11 pages). Order from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10017. A copy may be secured by citing the document number, remitting \$ 5.00 for photocopies or \$ 3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside the United States or Canada, postage is \$ 3.00 for a photocopy or \$ 1.00 for a fiche.

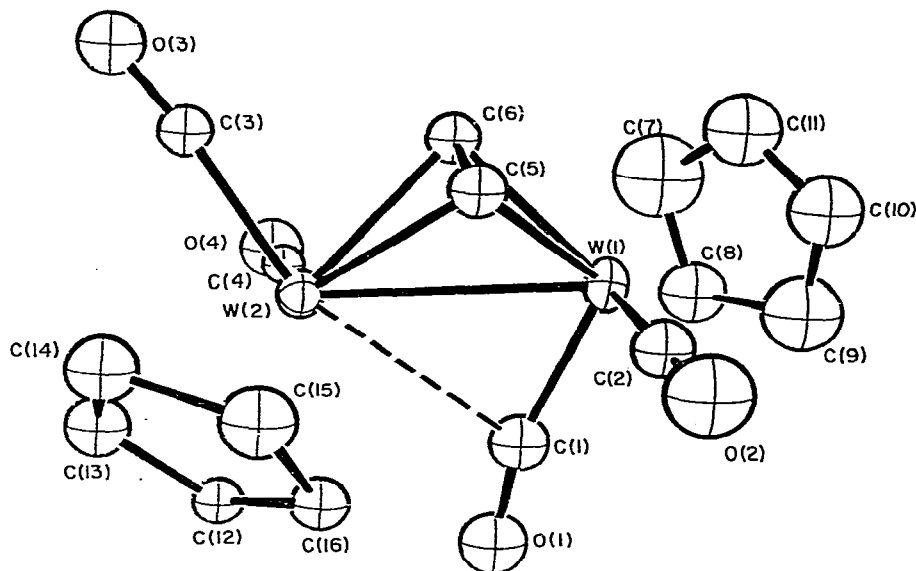


Fig. 1. The molecular geometry of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$.

TABLE 1

FINAL POSITIONS AND THERMAL PARAMETERS FOR $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B
W(1)	0.24629(11)	0.07799(5)	0.43068(11)	α
W(2)	0.23844(11)	0.24893(6)	0.48805(11)	α
C(1)	0.0700(28)	0.1130(15)	0.4040(26)	2.1(4)
C(2)	0.2151(36)	0.0530(19)	0.6414(36)	4.0(7)
C(3)	0.3943(22)	0.3142(14)	0.4752(26)	1.9(4)
C(4)	0.2161(26)	0.2561(14)	0.2635(27)	2.1(4)
C(5)	0.3889(29)	0.1665(15)	0.4324(24)	2.5(5)
C(6)	0.3670(26)	0.1579(14)	0.5819(26)	1.8(4)
C(7)	0.3159(46)	0.0430(24)	0.1878(45)	6.1(9)
C(8)	0.1925(38)	0.0148(20)	0.1876(37)	4.4(7)
C(9)	0.3072(39)	0.4633(21)	0.1803(39)	4.8(8)
C(10)	0.1712(43)	0.4614(21)	0.1213(40)	4.8(8)
C(11)	0.1043(40)	0.4994(21)	0.1975(40)	5.0(8)
C(12)	0.0295(29)	0.2896(15)	0.5146(29)	2.6(5)
C(13)	0.1081(33)	0.3573(17)	0.5328(32)	3.2(6)
C(14)	0.1964(36)	0.3426(18)	0.6748(36)	3.8(6)
C(15)	0.1556(31)	0.2653(16)	0.7326(30)	2.9(5)
C(16)	0.0555(27)	0.2390(15)	0.6391(27)	2.3(5)
O(1)	0.4620(24)	0.3695(12)	0.8730(23)	4.0(4)
O(2)	0.2127(29)	0.0384(15)	0.7763(30)	6.1(6)
O(3)	0.4840(21)	0.3562(11)	0.4681(20)	3.2(4)
O(4)	0.2078(22)	0.2612(12)	0.1271(22)	3.7(4)

α Anisotropic temperature factors: W(1): β_{11} 0.09540(12); β_{22} 0.00142(3); β_{33} 0.00890(15); β_{12} -0.00024(6); β_{13} 0.00017(7); β_{23} -0.00007(6). W(2): β_{11} 0.00340(11); β_{22} 0.00146(3); β_{33} 0.00791(14); β_{12} -0.00001(5); β_{13} 0.00020(8); β_{23} -0.00011(5). The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE 2

SELECTED DISTANCES (Å) AND ANGLES (°) OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ WITH STANDARD DEVIATION IN PARENTHESES

<i>(a) Interatomic distances</i>			
W(1)—W(2)	2.987(1)	C(5)—C(6)	1.33(3)
W(1)—C(1)	1.91(3)	W(2)—C(3)	1.97(3)
W(1)—C(2)	1.92(3)	W(2)—C(4)	1.94(2)
W(1)—C(5)	2.12(3)	W(2)—C(5)	2.18(3)
W(1)—C(6)	2.21(12)	W(2)—C(6)	2.17(2)
W(1)—C(7)	2.34(4)	W(2)—C(12)	2.30(3)
W(1)—C(8)	2.39(3)	W(2)—C(13)	2.35(3)
W(1)—C(9)	2.24(4)	W(2)—C(14)	2.34(3)
W(1)—C(10)	2.24(4)	W(2)—C(15)	2.35(3)
W(1)—C(11)	2.39(4)	W(2)—C(16)	2.38(3)
W(1)...C(3)	4.35(4)	W(2)...C(1)	2.97(3)
W(1)...C(4)	3.39(2)	W(2)...C(2)	3.64(3)
C(1)—O(1)	1.16(4)	C(3)—O(3)	1.18(3)
C(2)—O(2)	1.19(4)	C(4)—O(4)	1.18(3)
<i>(B) Interatomic angles</i>			
C(1)—W(1)—C(2)	87.5(13)	C(3)—W(2)—C(4)	86.6(10)
C(5)—W(1)—C(6)	35.8(9)	C(5)—W(2)—C(6)	35.7(9)
W(1)—C(5)—W(2)	87.9(11)	W(1)—C(6)—W(2)	86.0(9)
W(1)—C(1)—O(1)	172.9(21)	W(2)—C(3)—O(3)	177.0(22)
W(1)—C(2)—O(2)	171.5(32)	W(2)—C(4)—O(4)	177.2(24)
W(2)—W(1)—C(1)	70.8(8)	W(1)—W(2)—C(3)	121.5(7)
W(2)—W(1)—C(2)	93.2(10)	W(1)—W(2)—C(4)	84.2(7)
W(1)—C(1)—W(2)	71.7(8)	W(2)—C(1)—O(1)	112.5(18)

Å. While this part of the molecule, the W_2C_2 core, looks quite symmetrical, there is a single semi-bridging carbonyl group [C(1)O(1)] that makes the whole molecule asymmetrical and the environments about the two W atoms quite different.

The data support formulation of the C_2H_2 adduct as one containing essentially an M_2C_2 pseudotetrahedral core, as in other dimetal-acetylene complexes such as $\text{Co}_2(\text{CO})_6(\text{C}_2\text{R}_2)$ [6]. Thus, the schematic reaction (3) between two triple-bonded species seems reasonable. The W—W distance and the C(5)—C(6) distance also support the notion of a saturated complex. Some reference C—C and M—M distances are set out in Table 3. We see that in the $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4\text{-}(\text{C}_2\text{H}_2)$ complex the C(5)—C(6) bond is lengthened considerably from the 1.204 Å [5] in free C_2H_2 to a value of 1.33(3) Å which is close to that for the C—C bond ethylene. The bond lengthening is comparable to that found in $\text{Co}_2(\text{CO})_6\text{-}(\text{C}_2\text{R}_2)$ [6] (R = Ph, t-Bu) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_2\text{Ph}_2)$ [7] which also have the M_2C_2 tetrahedrane-like core. The W—W distance in the C_2H_2 adduct is shorter than in the parent $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$ [8]. Unfortunately, the structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$ has not been determined. But from the data for the Cr—Cr [9] and Mo—Mo [3] triple bonded species compared to their single bonded analogues [8], we can estimate the $\text{W}\equiv\text{W}$ distance in $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4$ to be 2.45 ± 0.01 Å, significantly less than that determined here for the C_2H_2 adduct (2.987(1) Å). Thus, it appears that some saturation of the $\text{W}\equiv\text{W}$ and the $\text{C}\equiv\text{C}$ bonds occurs adduct formation, but neither multiple bond is saturated to a representative single bond value. The Co—Co distance in $\text{Co}_2(\text{CO})_6(\text{C}_2\text{R}_2)$ [6] of ~ 2.47 Å is also shorter than the Co—Co distance in either $\text{Co}_2(\text{CO})_8$ (2.52)

TABLE 3
M—M AND C—C DISTANCES IN RELEVANT MOLECULES

Species	M—M (Å)	C—C (Å)	Reference
ethane		1.533	5
ethylene		1.334	5
acetylene		1.204	5
benzene		1.397	5
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$	3.235		8
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$	2.448		3
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{H}_2)$	2.984		4b
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{Et}_2)$	2.977		4a
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_6$	3.280		8b
$(\eta^5\text{-C}_5(\text{CH}_3)_5)_2\text{Cr}_2(\text{CO})_4$	2.280		9
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_6$	3.222		8
$(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$	2.987	1.33 (C ₂ H ₂)	This work
$\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$	2.47	1.369 (C ₂ Ph ₂)	6a, b
$\text{Co}_2(\text{CO})_6(\text{C}_2\text{-t-Bu}_2)$	2.463	1.335 (C ₂ -t-Bu ₂)	6c
$\text{Co}_2(\text{CO})_8$	2.52		10
$\text{Co}_2(\text{C}\text{O})_6(\text{P}(\text{n-Bu})_3)_2$	2.66		11
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{C}_2\text{Ph}_2)$	2.33	1.35	7
$(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CO})_2$	2.36		7

[10] or $\text{Co}_2(\text{CO})_6(\text{P}(\text{n-Bu})_3)_2$ (2.66 Å) [11]. These data parallel the present findings.

The most striking feature in $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ is the single semi-bridging carbonyl group, a feature which has also been observed by Cotton and co-workers in the closely related compounds $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{Et}_2)$ [4]. The presence of a single semi-bridging carbonyl group (SBCO) between two otherwise equivalent metal atoms runs contrary to intuitive expectations. To preserve symmetry, one would normally expect a complementary pair of SBCO's, one from each metal. In a recent article, Cotton and co-workers have made the plausible argument that the presence of the single SBCO in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ can be attributed to steric effects [4b].

The non-linearity of the W(1)—C(1)—O(1) angle in $(\eta^5\text{-C}_5\text{H}_5)_2\text{W}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ ($167(2)^\circ$) and the closeness of the W(2)...C(1) contact distance (2.97(3) Å, much shorter than the other three W...C distances which are all in excess of 3.3 Å), are both consistent with the idea that incipient bond formation is taking place between W(2) and C(1). There appears to be a hint of something like this occurring also in the triple-bond species $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2(\text{CO})_4$: their very low CO stretching frequencies indicate unusually large interactions between the carbonyl groups and the metal atoms. Indeed, the M'—M—C angles and the M'...C distances in these molecules (Table 4b) are comparable to those of semi-bridging carbonyl groups (Table 4a). It looks as though the CO orbitals in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cr}_2(\text{CO})_4$ are "bending over" to interact with the M≡M triple bond. This interaction could be in the form of enhanced back-donation from the electron density of the M≡M triple bond to the π^* orbitals of CO, combined perhaps with some OC → M donation from the C=O π bond to an appropriately empty metal orbital.

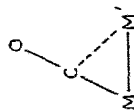


TABLE 4
COMPARISON OF THE STRUCTURAL PARAMETERS OF ($\eta^5\text{-C}_5\text{H}_5$)₂W₂(CO)₄(C₂H₂) WITH RELATED MOLECULES

Compound	M—M (Å)	M—C (Å)	M'...C (Å)	M'—M—C (°)	M—C—O (°)	IR bands (in alkanes) (cm ⁻¹)	Ref.
<i>(a) Molecules with a semi-bridging CO group</i>							
($\eta^5\text{-C}_5\text{H}_5$) ₂ W ₂ (CO) ₄ (C ₂ H ₂)	2.987(1)	1.91(3)	2.97(3)	70.8(8)	173(2)	1990, 1922, 1835	This work
($\eta^5\text{-C}_5\text{H}_5$) ₂ Mo ₂ (CO) ₄ (C ₂ H ₂)	2.984(1)		2.911(4)	—	—	1990, 1930, 1840	4b
($\eta^5\text{-C}_5\text{H}_5$) ₂ Mo ₂ (CO) ₄ (C ₂ H ₂)	2.997(1)	1.930(6)	2.826(6)	66.3	—	1997, 1930, 1852	4a
<i>(b) Molecules with a metal-metal triple bond</i>							
($\eta^5\text{-C}_5\text{H}_5$) ₂ Mo ₂ (CO) ₄	2.448(1)	2.13(5)	2.55(5)	67(1)	176(1)	1889, 1859	3
($\eta^5\text{-C}_5\text{Mo}_5$) ₂ Cr ₂ (CO) ₄	2.280(2)	1.842(6)	2.474(5)	73.0(3)	170.8(6)	1876, 1857	9
		1.822(5)	2.633(5)	79.1(3)	174.8(6)		

Assignment of electronic spectrum

The electronic spectra of $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4(\text{C}_2\text{H}_2)$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$) are shown in Fig. 2–4. The C_2H_2 adducts are remarkably similar to each other as are the parent hexacarbonyls. For all four compounds we find a low energy, low intensity visible absorption at ~ 500 nm, and in the near-UV we find a much more intense transition. The energy of the bands for $\text{M} = \text{W}$ are a little higher in energy than for $\text{M} = \text{Mo}$, and the near-UV transition for the C_2H_2 adducts is higher in energy than for the parent hexacarbonyls but the visible absorption maximum is at lower energy in the C_2H_2 adducts. The data are summarized in Table 5, and a common assignment for the absorption in the complexes appears appropriate.

The near-UV band in the hexacarbonyls has been assigned previously [12] to a metal-metal $\sigma_b \rightarrow \sigma^*$ transition. The position of the $\sigma_b \rightarrow \sigma^*$ absorption

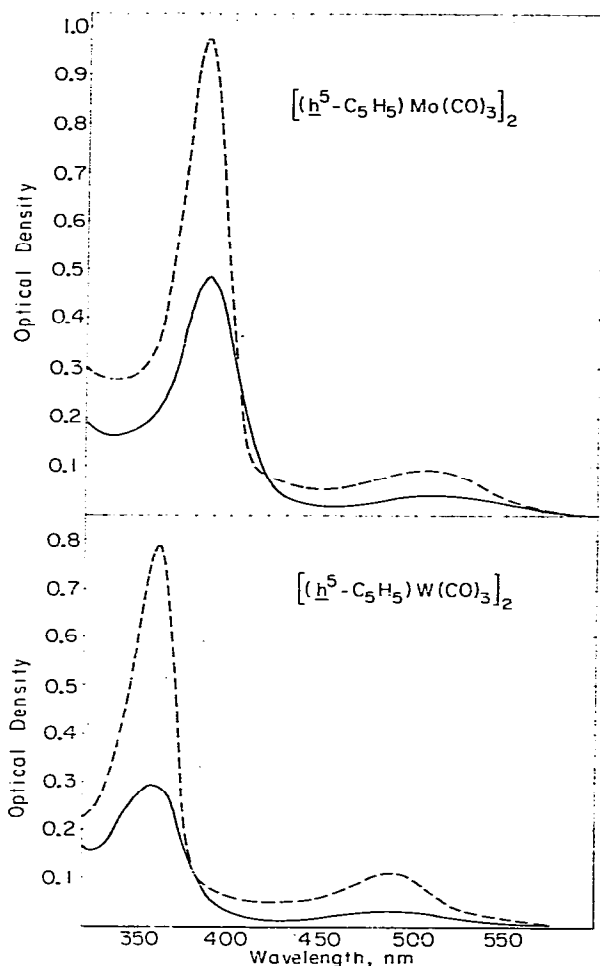


Fig. 2. Electronic spectra in EPA solution at 298 K (—) and upon cooling to 77 K (---). Spectral changes upon cooling are not corrected for solvent contraction. Band maxima and absorptivities in C_6H_6 at 298 K are given in Table 5.

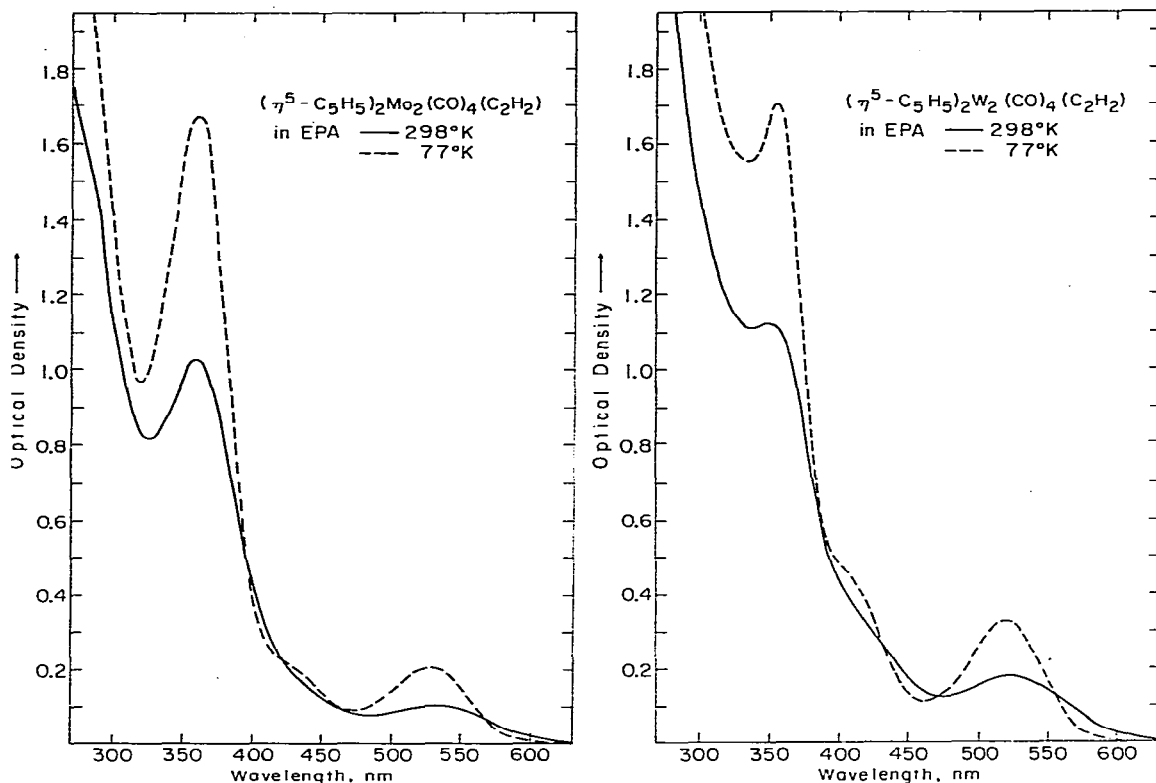


Fig. 3. Electronic spectra in EPA solution at 298 K (—) and upon cooling to 77 K (---). Spectral changes upon cooling are not corrected for solvent contraction. Band maxima and absorptivities in C_6H_6 at 298 K are given in Table 5. $M = Mo$.

Fig. 4. Electronic spectra in EPA solution at 298 K (—) and upon cooling to 77 K (---). Spectral changes upon cooling are not corrected for solvent contraction. Band maxima and absorptivities in C_6H_6 at 298 K are given in Table 5. $M = W$.

band has been correlated with bond dissociation energy [13], and thus a correlation for a given metal and metal-metal distance might be expected. Such a correlation does obtain, but it is curious that the shift to higher energy in the $\sigma_b \rightarrow \sigma^*$ absorption in the Mo complex is about twice as great as in the W complex. The position of the $\delta_b \rightarrow \delta^*$ absorption in a set of quadruple metal-metal

TABLE 5

ABSORPTION MAXIMA AND M-M DISTANCE IN $(\eta^5-C_5H_5)_2M_2(CO)_6$ AND $(\eta^5-C_5H_5)_2M_2(CO)_4(C_2H_4)^a$

Complex	M-M (Å)	$\sigma \rightarrow \sigma^*$ (cm^{-1}) (ϵ)	$\pi-d \rightarrow \sigma^*$ (cm^{-1}) (ϵ)
$(\eta^5-C_5H_5)_2Mo_2(CO)_6$	3.235 ^b	25,460 (23,200)	19,530 (2300)
$(\eta^5-C_5H_5)_2Mo_2(CO)_4(C_2H_4)$	2.984 ^c	27,700 (7400)	18,760 (850)
$(\eta^5-C_5H_5)_2W_2(CO)_6$	3.222 ^b	27,590 (21,000)	20,410 (2850)
$(\eta^5-C_5H_5)_2W_2(CO)_4(C_2H_4)$	2.987	28,370 (6000)	19,050 (900)

^a All spectral data are for 298 K C_6H_6 solutions recorded using a Cary 17 UV-vis-NIR spectrophotometer.

^b Ref. 8. ^c Ref. 4b.

bonded complexes was found to correlate with the M—M distance [14], and the shift in energy was of the order of 2000 cm^{-1} for a range of M—M distances of $\sim 2.0\text{--}2.2\text{ \AA}$. Consistent with a shift to higher energy for the M—M absorptions we note that the triple bonded $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4$ (M = Mo, W) species themselves do not have a low energy absorption attributable to a $\sigma_b \rightarrow \sigma^*$ transition [2] and we conclude that such an absorption is at substantially higher energy than for the single bonded $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$. The visible band in the C_2H_2 adducts, as in the parent hexacarbonyls, can be assigned to a $\pi\text{-}d \rightarrow \sigma^*$ transition. Thus, we can effectively treat the C_2H_2 adducts as $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4\text{L}_2$ derivatives of the parent hexacarbonyls with respect to their electronic spectral properties.

These electronic and geometrical structural considerations suggest a rich photochemistry for the C_2H_2 adducts involving metal—metal bond cleavage which is found [12,15—19] in other dinuclear carbonyl complexes exhibiting a low-lying $\sigma_b \rightarrow \sigma^*$ excitation. Preliminary experiments in one of our laboratories (M.S.W.) show the C_2H_2 adducts to be photosensitive, and the work will be published independently.

Acknowledgements

Research at M.I.T. was supported by the National Science Foundation and the Office of Naval Research. Research at USC was supported by National Science Foundation Grant CHE-74-01541. B.E.F. acknowledges the receipt of a fellowship from the Swiss National Science Foundation.

References

- 1 D.S. Ginley and M.S. Wrighton, *J. Amer. Chem. Soc.*, **97** (1975) 3533.
- 2 D.S. Ginley, C.R. Bock, and M.S. Wrighton, *Inorg. Chim. Acta*, **23** (1977) 85.
- 3 R.J. Klingler, W. Butler and M.D. Curtis, *J. Amer. Chem. Soc.*, **97** (1975) 3535.
- 4 (a) W.I. Bailey, Jr., F.A. Cotton, J.D. Jamerson and J.R. Kolb, *J. Organometal. Chem.*, **121** (1976) C23; (b) W.I. Bailey, D.M. Collins and F.A. Cotton, *ibid.*, **135** (1977) C53.
- 5 L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, New York, 1960, Chapt. 7.
- 6 (a) W.G. Sly, *J. Amer. Chem. Soc.*, **81** (1959) 18; (b) D.A. Brown, *J. Chem. Phys.*, **33** (1960) 1037; (c) F.A. Cotton, J.D. Jamerson and B. Stults, *J. Amer. Chem. Soc.*, **98** (1976) 1774.
- 7 O.S. Mills and B.W. Shaw, *J. Organometal. Chem.*, **11** (1968) 595.
- 8 (a) R.D. Adams, D.M. Collins and F.A. Cotton, *Inorg. Chem.*, **13** (1974) 1086; (b) R.D. Adams, D.M. Collins and F.A. Cotton, *J. Amer. Chem. Soc.*, **96** (1974) 749.
- 9 J. Potenza, P. Giordano, D. Mastropaolo and A. Efraty, *Inorg. Chem.*, **13** (1974) 2540.
- 10 G.G. Sumner, H.P. Klug and L.E. Alexander, *Acta Crystallogr.*, **17** (1964) 732.
- 11 J.A. Ibers, *J. Organometal. Chem.*, **14** (1968) 423.
- 12 M.S. Wrighton and D.S. Ginley, *J. Amer. Chem. Soc.*, **97** (1975) 4246.
- 13 J.P. Fawcett, A.J. Poë and M.V. Twigg, *J. Chem. Soc. Chem. Commun.*, (1973) 267.
- 14 A.P. Sattelberger and J.P. Fackler, *J. Amer. Chem. Soc.*, **99** (1977) 1258.
- 15 (a) M.S. Wrighton and D.S. Ginley, *J. Amer. Chem. Soc.*, **97** (1975) 2065; (b) D.S. Ginley and M.S. Wrighton, *ibid.*, **97** (1975) 4908; (d) D.L. Morse and M.S. Wrighton, *ibid.*, **98** (1976) 3931; (d) H.B. Abrahamson and M.S. Wrighton, *ibid.*, **99** (1977) 5510.
- 16 R.M. Laine and P.C. Ford, *Inorg. Chem.*, **16** (1977) 388.
- 17 C. Giannotti and G. Merle, *J. Organometal. Chem.*, **105** (1976) 97.
- 18 (a) J.L. Hughey, C.R. Bock and T.J. Meyer, *J. Amer. Chem. Soc.*, **97** (1975) 4440; (b) J.L. Hughey, IV, C.P. Anderson and T.J. Meyer, *J. Organometal. Chem.*, **125** (1977) C49.
- 19 B.H. Byers and T.L. Brown, *J. Amer. Chem. Soc.*, **97** (1975) 3270, 947.