MOLECULAR STRUCTURE OF THE Mo–Mo TRIPLE-BONDED PENTAMETHYLCYCLOPENTADIENYLMOLYBDENUM DIMER, $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$, AND ITS GEOMETRICAL RELATIONSHIP WITH THE NONMETHYLATED CYCLOPENTADIENYL ANALOGUE (Mo≡Mo) AND CORRESPONDING CHROMIUM DIMERS (Cr≡Cr)

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Summary

In order to determine whether the strikingly different chemical behavior of $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ (**1**) vs. $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ (**2**) is possibly linked to unusual variations in molecular structure, an X-ray crystallographic investigation of **1** has been carried out. This study revealed that the solid-state configuration of **1** is indeed distinctly different from that of **2** but that its Mo–Mo bond length is analogously short (at the high end of the triple-bond range). The centrosymmetrically-required geometry of **1** possesses a nonlinear $C_5Me_5(c)$–Mo–Mo' bond angle (where $C_5Me_5(c)$ denotes the ring centroid) of 168.3° and two markedly different pairs of linear-type semibridged carbonyls with one pair comparable to those in **2** but with the other pair much more asymmetric (corresponding to a considerably weaker interaction with the second molybdenum atom). In contrast, **2** experimentally conforms to a C_{2h}-$2/m$ geometry with a linear $C_5H_5(c)$–Mo–Mo'–$C_5H_5(c)$ axis and with its four carbonyl ligands equivalently bent back over the Mo–Mo bond in a linear-type semibridged arrangement. A crystal disordering in **1** of the less asymmetric-bridged carbonyl pair occurs in a similar fashion to that previously found and resolved for both asymmetric-bridged carbonyl pairs in **2**. The Mo–Mo triple-bond length of 2.488(3) Å in **1** is only 0.04 Å longer than that of 2.448(1) Å in **2** but 0.75 Å shorter than the weak, unbridged Mo–Mo single-bond distance of 3.235(1) Å in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6$. A comparative analysis of the geometrical variations in **1** and **2** is made with the corresponding structurally analogous $Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers (R = H, Me) and other semibridged carbonyl clusters in an effort to provide additional insight in assessing the current conflicting views on the bonding nature of the semibridged carbonyls in the $M_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers (M = Cr, Mo).

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Introduction

This structural analysis of $Mo_2(\eta^5-C_5Me_5)_2(CO)_4$ (1) was an outgrowth of our previous work involving a systematic investigation [1,2] of the chemical reactivity of the double-bonded metal–metal dimer, $Co_2(\eta^5-C_5Me_5)_2(\mu_2-CO)_2$ [3–5], with various photogenerated $M(CO)_x$ and $M(\eta^5-C_nR_n)(CO)_y$ species. This research [2,6] illustrated a rational synthetic route to new mixed-metal clusters via metal-fragment addition across a metal–metal multiple-bonded dimer. Five electronically equivalent, diamagnetic dicobalt-metal clusters containing a completely bonding metal triangle were prepared and characterized from spectral and X-ray diffraction measurements as members of two distinct series, viz., $MCo_2(\eta^5-C_5Me_5)_2(\mu_2-CO)_3(\mu_3-CO)$ (with $M = Cr(\eta^6-C_6H_5Me)$, $Mn(\eta^5-C_5H_4Me)$, $Fe(\eta^4-C_4H_4))$ and $MCo_2(\eta^5-C_5Me_5)_2(\mu_2-CO)_2(\mu_3-CO)$ (with $M = Fe(CO)_3$, $Co(\eta^5-C_5H_4Me))$. During the course of this investigation, we decided to expand its scope by a probing of the stereochemical consequences in reacting a triply-bonded metal–metal dimer with a variety of chemical substrates. Our choice of 1, whose reported chemical behavior [7,8] is virtually unexplored relative to the extensive, rich chemistry [9–25] exhibited by the corresponding unsubstituted cyclopentadienyl molybdenum dimer, $Mo_2(\eta^5-C_5H_5)_2(CO)_4$ (2), was made with the hope that from both electronic and steric considerations its pentamethylcyclopentadienyl rings would likewise dictate (as in the case of the above-mentioned cobalt dimer) the formation of new soluble stable mixed-metal clusters. The results of this highly fruitful research will be reported elsewhere [26,27].

First synthesized in 1967 by King and Bisnette [28] from the reaction of molybdenum hexacarbonyl with pentamethylcyclopentadiene in refluxing 2,2,5-trimethylhexane, this red crystalline dimer 1 was then postulated to possess a Mo–Mo triple bond in order to conform to the EAN rule. In 1971 King and Efraty [29,30] reported an alternate synthesis of this forerunner of the $Mo_2(\eta^5-C_5R_5)_2(CO)_4$ series along with the second member, $Cr_2(\eta^5-C_5Me_5)_2(CO)_4$, from the reaction of acetylpentamethylcyclopentadiene and the corresponding metal hexacarbonyl.

An X-ray crystallographic study [31,32] of $Cr_2(\eta^5-C_5Me_5)_2(CO)_4$ revealed a centrosymmetric molecule containing a short Cr–Cr bond length of 2.280(2) Å which is compatible with the previous formulation [29,30] of a triple bond between the chromium atoms. The linear-type semibridging orientation of the four carbonyl ligands was attributed [32] to nonbonded ligand repulsions. In an analogy to the previous utilization of steric arguments by Adams, Collins, and Cotton [33] to account for the observed geometry of the corresponding $Cr_2(\eta^5-C_5H_5)_2(CO)_6$ possessing an abnormally long Cr–Cr single-bond distance of 3.281(1) Å [33] compared to the Mo–Mo single-bond distance of 3.235(1) Å [34,35] in the isomorphous $Mo_2(\eta^5-C_5H_5)_2(CO)_6$, it was noted [32] that the determined Cr–Cr distance in $Cr_2(\eta^5-C_5Me_5)(CO)_4$ may likewise not represent the intrinsic strength of the Cr–Cr triple bond. In fact, it was suggested [32] that it would be of interest to determine the structure of 1 in order to determine the extent to which steric factors affect the Cr–Cr bond length in $Cr_2(\eta^5-C_5Me_5)_2(CO)_4$.

An extensive search was made by King, Efraty, and Douglas [7] for reactions of 1 and its chromium analogue involving addition to the metal–metal triple bond without cleavage; however, only mononuclear metal complexes were isolated, and hence they concluded that these dimers do not normally undergo addition reactions

without metal–metal bond scission. In 1975 Ginley and Wrighton [8] showed that carbon monoxide can be reversibly added to the metal–metal triple bond of **1** to give the corresponding Mo–Mo single-bonded $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_6$.

$Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ (**2**) was first isolated in low yield by Job and Curtis [36] in 1973 from the photolysis of $Mo(\eta^5\text{-}C_5H_5)(CO)_3(GeMe_2C_2H_3)$. The thermal conversion of $Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6$ to $Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ reported by Manning and co-workers [37] in 1974 was soon followed by publications on the analogous formation of **2** from $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6$ via photolysis by Wrighton and Ginley [38] and via thermolysis by Klingler, Butler, and Curtis [11]. Both groups [8,12,17,38] showed that the mechanism of generation of $M_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ (M = Cr, Mo, W) and $M_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ (M = Cr, Mo) from the corresponding metal–metal single-bonded $M_2(\eta^5\text{-}C_5R_5)_2(CO)_6$ dimers by either irradiation or heating involves cleavage of the metal–metal single bond. Pioneering work by Curtis and co-workers [11–16] established that the chemical properties of **2** are remarkably different from those in **1**, in that **2** readily undergoes a variety of nucleophilic and electrophilic additions with concomitant reduction in the Mo–Mo bond order without cleavage of the dimeric unit. Curtis and Klingler [12] also showed that **2** gives rise to metal-cluster formation by reaction with a number of transition metal carbonyl species but due to instability and/or insolubility problems the resulting products were characterized by only elemental and spectroscopic analyses.

From an X-ray crystallographic study of the structure of **2**, Klingler, Butler, and Curtis [11,39] proposed that the determined semibridging carbonyl positions are a consequence of the carbonyl ligands functioning as incipient four-electron donors. Curtis and Butler [40] also performed a structural determination of $Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ by X-ray crystallography in order to relate their proposed semibridging carbonyl bonding model to both $Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers (R = H, Me). However, a molecular orbital investigation of **2** by Jemmis, Pinhas, and Hoffmann [41] and an extensive analysis by Colton and McCormick [42] of the known crystal structures involving μ_2-bridging carbonyls in transition metal complexes have given rise to different views concerning the nature of the semibridging carbonyls in the $M_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers.

This need for further experimental and theoretical scrutiny of the $M_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers coupled with a desire to find out whether the pronounced chemical differences between **1** and **2** may be related to unusual geometrical variations furnished further incentives (in addition to our particular interest in connection with a stereochemical investigation of the reactions of **1** with various transition metal substrates to produce new mixed-metal clusters) for the crystallographic determination of **1** and the comparative structural analysis reported herein.

Experimental

Preparation and characterization of 1

This dimer was synthesized by the preparative route described by King et al. [43] involving the reflux reaction of $Mo(CO)_6$ and pentamethylcyclopentadiene in n-decane followed by chromatographic separation on a Florisil column of the crystallized mixture redissolved in dichloromethane. The first reddish band eluted with diethyl ether/hexane was identified as **1** from its characteristic IR spectral pattern of two strong carbonyl frequencies in both toluene solution and in KBr pellet being in close

TABLE 1. ATOMIC PARAMETERS FOR $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$

Positional parameters

Atom	x	y	z
Mo	0.0199(2)	0.0770(2)	0.4511(1)
O(1)	0.3256(16)	0.2110(16)	0.6059(7)
O(2) [a]	−0.2482(18)	0.2559(16)	0.4997(8)
C(1)	0.2172(24)	0.1476(22)	0.5533(11)
C(2) [a]	−0.1649(26)	0.1644(32)	0.4922(15)
Cp(1)	−0.0258(28)	0.0371(21)	0.3282(9)
Cp(2)	0.1497(25)	0.1044(23)	0.3711(9)
Cp(3)	0.1390(22)	0.2554(24)	0.3950(9)
Cp(4)	−0.0434(27)	0.2915(22)	0.3682(10)
Cp(5)	−0.1469(20)	0.1593(26)	0.3271(9)
Cp(6)	−0.0764(42)	−0.1232(26)	0.2882(13)
Cp(7)	0.3207(28)	0.0193(32)	0.3833(13)
Cp(8)	0.2994(28)	0.3729(27)	0.4369(12)
Cp(9)	−0.1194(38)	0.4556(25)	0.3766(16)
Cp(10)	−0.3586(23)	0.1507(29)	0.2853(11)

Anisotropic thermal parameters $(\times 10^4)$ [b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	248(4)	204(3)	31(1)	3(3)	39(1)	9(1)
O(1)	243(26)	276(28)	51(1)	−40(23)	17(9)	−43(10)
O(2)	308(31)	246(26)	83(7)	22(26)	103(13)	−14(11)
C(1)	220(36)	183(31)	66(9)	12(28)	53(15)	−36(14)
C(2)	208(40)	416(60)	99(14)	72(42)	47(19)	−115(25)
Cp(1)	368(50)	204(35)	36(6)	−83(34)	58(14)	−18(11)
Cp(2)	307(43)	232(37)	34(6)	51(33)	49(13)	18(12)
Cp(3)	246(38)	251(37)	36(6)	17(32)	45(12)	23(12)
Cp(4)	347(50)	168(31)	44(7)	−3(32)	30(15)	21(12)
Cp(5)	146(28)	296(41)	34(6)	−41(29)	−1(10)	7(3)
Cp(6)	775(108)	208(40)	67(11)	−23(52)	139(29)	−39(17)
Cp(7)	298(47)	360(51)	83(11)	107(43)	96(20)	−7(21)
Cp(8)	286(44)	308(45)	62(9)	−81(38)	55(17)	−22(17)
Cp(9)	564(83)	207(43)	102(15)	95(45)	152(31)	11(18)
Cp(10)	174(32)	403(53)	59(9)	14(36)	30(14)	22(18)

[a] The coordinates of C(2) and O(2) designate crystal-disordered mean positions, each of which is a whole-weighted composite of two half-weighted semibridging carbonyl components. [b] Anisotropic temperature factors are of the form $\exp\{-[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]\}$.

agreement with those of 1867 and 1842 cm^{-1} in n-tetradecane solution reported by King et al. [43]. Crystals were obtained from solvent diffusion of a toluene/hexane solution.

X-Ray data collection, crystal data, structural determination, and refinement

After examination of a number of crystals, a red parallelepiped-shaped one of dimensions $0.50 \times 0.40 \times 0.25$ mm was affixed to the end of a glass fiber and then mounted inside a Lindemann glass capillary which was evacuated, filled with argon, and then hermetically sealed. X-Ray data were obtained at 22°C over the range

TABLE 2

INTRAMOLECULAR DISTANCES AND BOND ANGLES FOR $Mo_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ (1) [a,b]

Intramolecular distances (Å)

Mo–Mo′	2.488(3)	Cp(1)–Cp(6)	1.514(26)
Mo–C(1)	2.010(19)	Cp(2)–Cp(7)	1.513(26)
Mo–C(2)	2.193(21)	Cp(3)–Cp(8)	1.551(26)
Mo′–C(2)	2.351(28)	Cp(4)–Cp(9)	1.557(27)
Mo′···C(1)	2.707(19)	Cp(5)–Cp(10)	1.564(22)
Mo···O(1)	3.137(12)		1.540(av)
Mo′···O(1)	3.516(14)		
Mo···O(2)	3.210(13)	*Bond angles* (deg)	
Mo′···O(2)	3.255(14)	Mo′–Mo–C(1)	73.1(6)
C(1)···C(2)	2.840(26)	Mo′–Mo–C(2)	59.9(8)
C(1)–O(1)	1.141(19)	Mo–Mo′–C(2)	53.8(6)
C(2)–O(2)	1.094(20)	Mo–C(2)–Mo′	66.3(9)
Mo–Cp(c) [c]	1.993	Mo–C(1)–O(1)	169.1(18)
Mo–Cp(1)	2.317(16)	Mo–C(2)–O(2)	153.5(26)
Mo–Cp(2)	2.330(17)	Mo′–C(2)–O(2)	138.8(25)
Mo–Cp(3)	2.352(16)	Cp(c)–Mo–Mo′	168.3
Mo–Cp(4)	2.324(17)	Cp(c)–Mo–C(1)	118.3
Mo–Cp(5)	2.294(15)		
	2.323(av)	Cp(1)–Cp(2)–Cp(3)	110.8(17)
Cp(1)–Cp(2)	1.421(26)	Cp(2)–Cp(3)–Cp(4)	107.9(17)
Cp(2)–Cp3	1.368(24)	Cp(3)–Cp(4)–Cp(5)	108.4(18)
Cp(3)–Cp(4)	1.392(25)	Cp(4)–Cp(5)–Cp(1)	108.4(15)
Cp(4)–Cp(5)	1.404(24)	Cp(5)–Cp(1)–Cp(2)	104.5(15)
Cp(5)–Cp(1)	1.434(27)		108.0(av)
	1.404(av)		
Cp(6)–Cp(1)–Cp(5)	127.2(19)		
Cp(6)–Cp(1)–Cp(2)	128.2(21)		
Cp(7)–Cp(2)–Cp(1)	122.9(19)		
Cp(7)–Cp(2)–Cp(3)	126.3(19)		
Cp(8)–Cp(3)–Cp(2)	126.1(17)		
Cp(8)–Cp(3)–Cp(4)	125.7(18)		
Cp(9)–Cp(4)–Cp(3)	125.5(19)		
Cp(9)–Cp(4)–Cp(5)	125.9(19)		
Cp(10)–Cp(5)–Cp(4)	125.3(20)		
Cp(10)–Cp(5)–Cp(1)	126.3(18)		
	125.9(av)		

[a] The primed atoms denote those related by the crystallographic center of symmetry at 0, 0, 1/2. [b] Since the coordinates of C(2) represent a crystal-disordered, whole-weighted mean carbon peak which was not resolved into its half-weighted components, all distances and bond angles involving C(2) are not reliable. Molecular parameters involving O(2) are assumed to be more reliable in that the size and shape of its thermal ellipsoid (relative to those of the other atoms) along with statistically equivalent Mo···O(2) and Mo′···O(2) distances indicate that the corresponding half-weighted oxygen atoms are nearly superimposed. [c] Cp(c) designates the centroid, $C_5Me_5(c)$, of the pentamethylcyclopentadienyl ring.

$5° < 2\theta < 50°$ via the ω scan mode with Mo-K_α radiation on a Syntex (Nicolet) $P\bar{1}$ diffractometer. Details of the crystal alignment and data collection parameters together with a listing of the utilized crystallographic programs are given elsewhere [44]. The dimer (M = 574) crystallizes in a monoclinic unit cell with $P2_1/c$ symmetry and dimensions a 8.383(4), b 8.365(3), c 19.936(5) Å, β 118.33(3)°, and V 1230.5(8) Å^3. The calculated density is 1.55 g cm^{-3} for $Z = 2$.

For this cell, data reduction gave 1621 observed reflections ($I > 2\sigma(I)$) which were empirically corrected for absorption via the ψ scan technique. Initial coordinates for the nonhydrogen atoms (corresponding to one-half dimer as the crystallographic independent unit) were obtained via the heavy-atom Patterson method followed by repeated Fourier syntheses; full-matrix least-squares refinement (which included anomalous dispersion corrections of the atomic scattering factors) with anisotropic thermal parameters for all nonhydrogen atoms converged at $R_1(F)$ 9.8% and $R_2(F)$ 15.0%. These relatively high discrepancy factors can be readily attributed to a twinning problem which affects the observed intensities. This difficulty involving a crystal-twinned mirror component was recognized during the crystallographic analysis such that the initially selected monoclinic unit cell of dimensions a' 8.383(4), b' 8.365(3), c' 35.161(8) Å, β' 93.52(2)°, and V'' 2461.0(1.5) Å^3 (with $Z = 4$) and of $P2_1$ (or $P2_1/m$) symmetry, was transformed by $a = a'$, $b = b'$, $c = -a' + c'/2$ (with $V = V'/2$) to the unit cell of $P2_1/c$ symmetry. Fortunately, the intensities due to the crystal-twinned mirror component were relatively weak, and our satisfaction with the refined crystal structure results from its determined geometry possessing reasonable metal–ligand and ligand–ligand distances and bond angles which compare favorably with corresponding values for related structures.

A final Fourier difference map showed no anomalous features. Atomic parameters for **1** are given in Table 1 and appropriate interatomic distances and bond angles in Table 2.

Results and discussion

Description of the molecular structure of *1*

Its crystal-disordered molecular configuration is viewed in Fig. 1. There is no indication from a crystal packing analysis, which revealed no close contacts between neighboring molecules, of any unusual intermolecular interactions that might abnormally influence the molecular geometry of **1** in the solid state.

Figure 1 indicates that the overall architecture of **1** consists of two identical $Mo(\eta^5\text{-}C_5Me_5)(CO)$ moieties linked to each other by two carbonyl bridges and by direct Mo–Mo bonding. To a first approximation the entire molecular configuration of crystallographic $C_i - \bar{1}$ site symmetry conforms to $C_{2h} - 2/m$ symmetry with the mirror plane passing through the two Mo atoms and two pseudo-terminal carbonyl ligands and with the perpendicular twofold axis directed through the two bridging carbonyl ligands.

A striking structural feature revealed in Fig. 1 is that the thermal ellipsoid of the bridging carbonyl atom C(2) is unusually elongated along the Mo–Mo' bond direction relative to that of the corresponding carbonyl oxygen atom O(2). The sizes, shapes, and orientations of the thermal ellipsoids of C(2) and O(2) are readily interpreted as a composite of two equally probable orientations of one crystal-disordered linear-type bridging carbonyl ligand from each Mo atom being asymmetrically coordinated to the other Mo atom. The nondisordered molecule thereby is assumed to possess only an inversion center with the above-mentioned mirror plane producing a random distribution of each dimer in one of two orientations in the crystal. This resulting crystal disorder of only one of the two carbonyl ligands per Mo atom is in complete harmony with the previous interpretation by Curtis and coworkers [11,29] of a similar type of crystal disorder observed in the corresponding
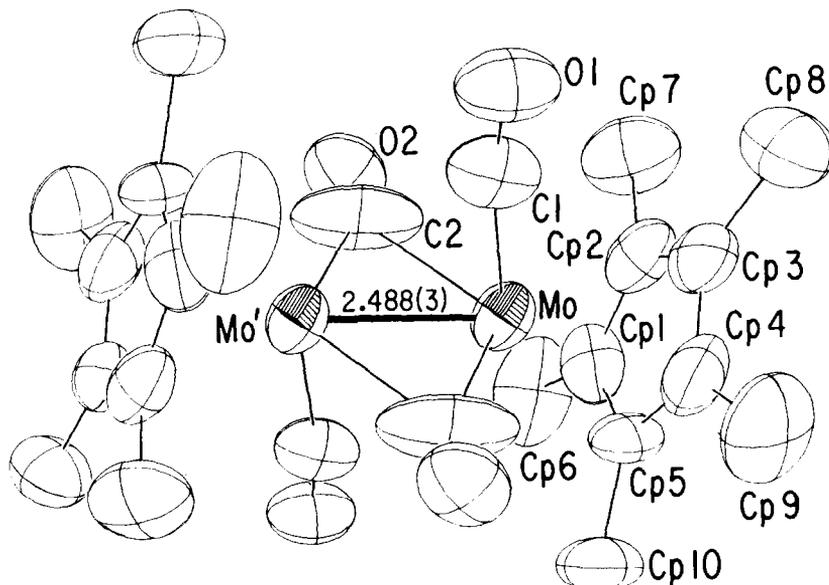
Fig. 1. The crystal-disordered molecular configuration of $Mo_2(\eta^5-C_5Me_5)_2(CO)_4$ (1), which possesses crystallographic $C_i - \bar{1}$ site symmetry, approximately conforms to $C_{2h} - 2/m$ symmetry with the mirror plane passing through Mo, Mo', and the pseudo-terminal carbonyl ligand C(1)–O(1). The unusual elongation along the Mo–Mo' direction of the thermal ellipsoid of the bridging carbonyl C(2) peak relative to that of the corresponding O(2) peak is a consequence of these crystal-disordered mean positions being a composite of two half-weighted linear-type semibridging carbonyl components whose oxygen atoms are nearly superimposed at O(2). The non-disordered dimer 1 is then assumed to have only an inversion center with the mirror plane giving rise to a random distribution of each dimer in one of two unit-cell orientations which thereby produces the observed crystal-disordered molecular geometry.

unsubstituted cyclopentadienyl molybdenum dimer, 2, involving in this case both carbonyl ligands per Mo atom forming an analogous asymmetric bridging system (vide infra).

Stereochemical relationship 1 with 2 and the $Cr_2(\eta^5-C_5R_5)_2(CO)_4$ dimers (R = H, Me) and resulting bonding implications

General comments. A comparison of the solid-state configuration of 1 with that of the previously structured 2 reveals a similarly short Mo–Mo' bond length together with highly distinct geometrical differences involving a markedly different disposition of $C_5Me_5^-$ and CO ligands about the Mo–Mo bond.

Metal–metal bonding

The Mo–Mo bond length of 2.488(3) Å in 1 is only 0.04 Å longer than that of 2.448(1) Å [11,39] in 2 but 0.75 Å shorter than that of 3.235(1) Å [35] for the unbridged Mo–Mo electron-pair bond in $Mo_2(\eta^5-C_5H_5)_2(CO)_6$. These bond length variations are consistent with the Mo–Mo bond in 1 being likewise regarded as a triple bond. In fact, the Mo–Mo distances for these d^5 Mo(I) dimers are analogous to the Mo–Mo triply-bonded distance of 2.457(1) Å found in the ligand-bridged d^5 Mo(I) $Mo_2[F_2PN(Me)PF_2]_4Cl_2$ dimer [45] but are 0.25–0.3 Å longer than those determined for several typical unbridged d^3 Mo(III) Mo_2X_6 dimers (X = CH_2SiMe_3 [46], NMe_2 [47], and OCH_2CMe_3 [48]).

The Mo–Mo bond length trend between **1** and **2** is also paralleled in the corresponding $Cr_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers in that the Cr–Cr bond length of 2.280(2) Å [32] in the permethylcylopentadienyl chromium analogue is slightly but significantly longer than those of 2.230(3) and 2.200(3) Å [40] in the two crystallographically independent molecules of $Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4$. These short Cr–Cr bond lengths have similarly been considered [29–32,40] in terms of a formal metal–metal bond order of 3.0. In contrast to the long Mo–Mo single bond of 3.235(1) Å [35] in $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6$ being anomalously shorter (by 0.05 Å) than the unusually long and (no doubt) strained single bond of 3.281(1) Å [33] in the sterically crowded, isostructural $Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6$, the fact that the observed Mo–Mo bond length in **1** is expectedly longer (by 0.21 Å) than the Cr–Cr bond length in $Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ points to the above-mentioned metal–metal bond lengths for the $M_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers (M = Cr, Mo; R = H, Me) not being markedly influenced by nonbonded repulsive forces between the ligands.

Ligand arrangement about the dimetal core

Major architectural differences exist between **1** and **2** in the crystalline state. Whereas in **2** the $C_5H_5^-$ rings are oriented to give a linear $C_5H_5(c)$–Mo–Mo′–$C_5H_5(c)′$ axis and all four carbonyls are equivalently bent back over the Mo–Mo bond to form linear-type asymmetric bridges [11,39], in **1** the two centrosymmetrically related $C_5Me_5^-$ rings are nonlinear with the Mo–Mo axis (corresponding to a $C_5Me_5(c)$–Mo–Mo′ bond angle of 168.3°) and the degree of semibridging is markedly different for the two pairs of carbonyl ligands.

In **1** the crystallographically independent, nondisordered C(1)–O(1) peaks, which give rise to a nearly linear Mo–C(1)–O(1) bond angle of 169(2)°, may be described as a highly asymmetric bridge in that the Mo–C(1) and Mo′–C(1) distances of d_1 2.01(2) Å and d_2 2.71(2) Å, respectively, correspond to an α value (where $\alpha = (d_2 - d_1)/d_1$ [39]) of 0.35 which is considerably larger than that of 0.20 (av) for the four experimentally equivalent semibridging carbonyls in **2**. This much weaker interaction of C(1)–O(1) with the second metal, Mo′, is also reflected in the Mo′–Mo–C(1) bond angle of 73.1(6)° being significantly larger than those of 67° (av) for the four semibridging carbonyls in **2**.

In **1** the crystallographically independent, disordered C(2)–O(2) peaks were not resolved into two mirror-related half-weighted carbonyl components. Nevertheless, a rough estimate of the degree of asymmetry of an individual carbonyl component with Mo′ may be obtained on the basis of an assumed linearity of the Mo–C(2)–O(2) bond angle coupled with the additional assumption that the O(2) peak, which is essentially equidistant (viz., 3.23 Å (av)) from both Mo atoms, represents the whole-weighted superposition of the two half-weighted oxygen atoms. These compensating assumptions give rise to a calculated Mo′···CO distance of 2.56 Å and a Mo′–Mo–CO bond angle of 67° which are not unlike those in **2**.

Since electronic considerations do not appear to provide a clearcut explanation to account for these geometrical variations in ligand arrangement between **1** and **2**, one may invoke steric effects as the probable cause.

On the other hand, the solid-state structure [31,32] of the corresponding centrosymmetric $Cr_2(\eta^5\text{-}C_5Me_5)_2(CO)_4$ is closely related to that [33] of the $Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_4$ (for which there are two crystallographically independent centrosymmetric molecules). In each centrosymmetric dimer all four carbonyls are also bent

back over the Cr–Cr bond in linear-type semibridging positions (without any crystal disorder) and the *trans*-$C_5R_5^-$ rings are similarly oriented with analogous $C_5R_5(c)$–Cr–Cr' angles of 158.7° in the pentamethylcyclopentadienyl derivative vs. 158.7 and 165.0° for the two independent $Cr_2(\eta^5-C_5H_5)_2(CO)_4$ molecules.

The greater asymmetry of the semibridging carbonyls in both $Cr_2(\eta-C_5Me_5)_2(CO)_4$ and $Cr_2(\eta^5-C_5H_5)_2(CO)_4$ compared to that in 2 (associated with considerably smaller carbonyl bonding interactions with Cr' than with Mo') is evidenced by the significantly larger Cr'–Cr–CO bond angles for the two independent carbonyls in the centrosymmetric $Cr_2(\eta^5-C_5Me_5)_2(CO)_4$ (73.0(3) and 79.1(3)°) [32] and in each of the independent centrosymmetric molecules of $Cr_2(\eta^5-C_5H_5)_2(CO)_4$ (74.7(3) and 75.2(3)° in one molecule and 72.2(4) and 72.4(3)° in the other) [40].

Bonding nature of the semibridged carbonyl ligands

Both the origin and bonding mode of the linear-like semibridged carbonyls in these $M_2(\eta^5-C_5R_5)_2(CO)_4$ dimers (M = Cr, Mo; R = H, Me) are still subject to different views [13,16,39–42]. On the basis of a detailed crystallographic analysis of the nature of asymmetry in bent vs. linear carbonyl bridging systems, Curtis and co-workers [39] proposed that the observed linear-type semibridging carbonyls found in 2, in $Cr_2(\eta^5-C_5R_5)_2(CO)_4$ (R = H, Me) and in $V_2(\eta^5-C_5H_5)_2(CO)_5$ [49] may be rationalized in terms of each carbonyl ligand being considered as an incipient four-electron donor by virtue of electron donation from one of its $1\pi(CO)$ orbitals to the second metal atom. They pointed out that this $(\sigma + \pi)$ bonding mode for each semibridging carbonyl ligand would be expected to increase the metal–metal bond length. In the case of 2, they suggested that conceptually it was realistic to think of its Mo–Mo bond as a triple bond which has been lengthened slightly by a bonding interaction with the bridging carbonyls. In contradistinction to a previous interpretation [32] which ascribed the carbonyl positions in $Cr_2(\eta-C_5Me_5)_2(CO)_4$ to intramolecular steric effects, Curtis and Butler [40] instead suggested that the observed geometries of 2 and of both $Cr_2(\eta-C_5R_5)_2(CO)_4$ dimers (R = H, Me) are a consequence of electronic $1\pi(CO)$-to-$d\pi(M)$ interactions.

Subsequent EHMO calculations carried out by Hoffmann and co-workers [41] on 2 indicated for its observed geometry a replacement of Mo–Mo multiple bonding by compensating metal carbonyl interactions which involve the occupied metal-based orbitals acting as donors to the $\pi^\star(CO)$ acceptor orbitals; this latter model is consistent with Cotton's original proposal [50] of the electronic character of semibridging carbonyls. The indicated $d\pi(Mo)$-to-$\pi^\star(CO)$ charge transfer was revealed from an overlap population analysis [41] with antibonding Mo $\cdots$ O interactions coupled with bonding Mo $\cdots$ C interactions.

Strong stereochemical evidence that a linear-type semibridging carbonyl or isoelectronic cyanide ligand can indeed be a four-electron donor was provided by Curtis et al. [12] from their structural determination of the $[Mo_2(\eta^5-C_5H_5)_2(CO)_4(\sigma,\pi-CN)]^-$ monoanion, an adduct from the reaction of 2 with cyanide ion. Their assumption that the linear-type cyanide ligand (which is crystallographically disordered in two overlapping orientations in a presumably analogous fashion to the crystal disorder of the semibridging carbonyls in 1 and 2) donates a total of four electrons to the two molybdenum atoms via a $(\sigma + \pi)$ bonding mode is supported from electronic considerations by the resulting Mo–Mo distance of 3.139(2) Å being consistent with a Mo–Mo single bond. The sharply acute

Mo'–Mo–CN bond angle of 49° (av) reflects their proposed strong $1\pi(CO)$-to-$d\pi(Mo')$ interaction. A similar $(\sigma + \pi)$ semibridged bonding mode is likewise encountered in the electronically equivalent and geometrically similar 1 : 1 isocyanide adducts $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\sigma,\pi\text{-}CNR)$ (with R = Me, Ph, t-Bu) [18]; an X-ray diffraction study by Adams and coworkers [18] of the phenyl isocyanide adduct revealed that the four-electron donating $\mu_2\text{-}\eta^2$-isocyanide ligand likewise gives rise to a Mo–Mo single-bond distance (3.212(1) Å). Another prominent example of a structurally analogous adduct possessing a $(\sigma + \pi)$-coordinated semibridged ligand is the related $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\sigma,\pi\text{-}NCNMe_2)$ [19], in which the Mo–Mo distance of 3.056(1) Å also corresponds to a single bond. In this dimer the asymmetrically bridged dimethylaminocyanamide ligand (which forms a Mo'–Mo–N bond angle of 44.6(2)°) was described by Chisholm, Cotton, et al. [19] as being coordinated to the two molybdenum atoms via σ-donation of a nitrogen lone pair to one Mo atom and a $\pi(NC)$ electron-pair donation to the other Mo atom. Other metal clusters also possessing linear-type semibridging carbonyls which function as either 4- or 6-electron donors include: (1) $Mn_2(CO)_4(\sigma,\pi\text{-}CO)(Ph_2PCH_2CH_2PPh_2)$ [51–53] and $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\sigma,\pi\text{-}CO)Nb(\eta^5\text{-}C_5H_5)_2$ [54] where in each molecule the observed metal–metal single-bonded distance can be readily rationalized on the basis of a presumed $1\pi(CO)$-to-$d\pi(M)$ donor interaction from the coordination of one linear-type semibridging carbonyl to the second metal atom; (2) the $[Fe_4(CO)_{13}H]^-$ monoanion [55] which exhibits a butterfly metal core with a 4-electron donating ($\mu_4\text{-}C$, $\mu_1\text{-}O$) carbonyl bridge; and (3) $Nb_3(\eta^5\text{-}C_5H_5)_3(CO)_7$ [56,57] in which one carbonyl appears to act as a 6-electron donating ($\mu_3\text{-}C$, $\mu_2\text{-}O$) bridge.

In a recent comprehensive survey of μ_2-bridging carbonyl systems in transition metal complexes, Colton and McCormick [42] reject the proposal by Curtis and co-workers [16,39] that the four carbonyls in **2** function as incipient four-electron donors on the grounds that the Mo–C bridge bonds differ by ca. 0.5 Å and that the carbonyl stretching frequencies of 1900 and 1850 cm^{-1} are close to normal terminal values. Instead, they prefer to classify the carbonyls in **2** as "borderline semibridging". Moreover, their general conclusion is that the type of carbonyl bridge observed in the crystalline state is largely a result of intramolecular and intermolecular steric forces rather than predominately due to electronic effects.

Conclusions

The intriguing, diverse reactivity patterns displayed [9–25] for **2** vs. the limited ones found [7,8] for **1** may be attributed not only to the bulky methyl ring substituents in **2** restricting access of chemical substrates to the metal sites but also to differences in energetics associated with their different geometries. Unfortunately, the above stereochemical analysis does not clarify the conflicting views [16,39,41,42] concerning the bonding nature of the semibridged carbonyls in the $M_2(\eta^5\text{-}C_5R_5)_2(CO)_4$ dimers (M = Cr, Mo; R = H, Me). The fact that the Mo–Mo bond lengths in **1** and **2** are in the triple-bond range (although at the high end [58]) rather than in the single-bond range indicates that the semibridged carbonyls in **1** and **2** are at most incipient (or very weak) $1\pi(CO)$ electron-pair donors. Similarly, the existence of much shorter Cr–Cr bond lengths in both chromium analogues, for which the carbonyl bridges are more asymmetric, is consistent with an even much weaker $1\pi(CO)$ donor interaction (and analogously weaker $\pi^*(CO)$ backbonding interaction) of each carbonyl with the second metal atom. The presence of four equivalent

semibridged carbonyls in **2** vs. only two comparable ones in **1** (with its other two being much more asymmetric) does not result in the Mo–Mo bond in **1** being shorter than that in **2**. In light of the aforementioned bonding conclusions derived from the MO study of **2** by Hoffmann and co-workers [41], it is evident that further theoretical investigations of **1** and related carbonyl-bridged complexes should be performed to amplify from a comparative analysis the electronic structures of these molecules.

Finally, we wish to reemphasize our long-standing prejudice, which is apparently contrary to the above-stated beliefs of Colton and McCormick [42], that electronic effects do play an important role in dictating the geometries of a number of carbonyl-bridged systems. For example, the molecular dissimilarity of the (triangular metal)-bonding $Rh_3(\eta^5\text{-}C_5H_5)_3(CO)(C_6H_5C_2C_6H_5)$ and $Rh_3(\eta^5\text{-}C_5H_5)_3(CO)\text{-}(C_6F_5C_2C_6F_5)$ homologues [59], which primarily differ from each other by coordination of the bridging carbonyl to the three Rh atoms in the former molecule and to two Rh atoms in the latter molecule, can be readily rationalized [59] from qualitative bonding considerations on the basis of electronic effects involving the nature of the acetylene substituents. The indication from infrared carbonyl data [59] that the different molecular geometries of the two homologues remain unchanged upon dissolution of the crystalline materials restricts the Colton-McCormick feeling [42] "that steric forces are also responsible for their appearance in the solid state" to intramolecular forces which we deem unlikely in this case.

Acknowledgments

References

1 L.M. Cirjak, R.E. Ginsburg and L.F. Dahl, J. Chem. Soc., Chem. Commun., (1979) 470.
2 L.M. Cirjak, Jin-Shun Huang, Zhong-He Zhu and L.F. Dahl, J. Amer. Chem. Soc., 102 (1980) 6623.
3 R.E. Ginsburg, L.M. Cirjak and L.F. Dahl, J. Chem. Soc., Chem. Commun., (1979) 468.
4 W.I. Bailey, Jr., D.M. Collins, F.A. Cotton, J.C. Baldwin and W.C. Kaska, J. Organometal. Chem., 165 (1979) 373.
5 L.M. Cirjak, R.E. Ginsburg and L.F. Dahl, Inorg. Chem., 21 (1982) 940.
6 L.M. Cirjak, Jin-Shun Huang, Zhong-He Zhu and L.F. Dahl, to be published.
7 R.B. King, A. Efraty and W.M. Douglas, J. Organometal. Chem., 60 (1973) 125.
8 D.S. Ginley and M.S. Wrighton, J. Am. Chem. Soc., 97 (1975) 3533.
9 F.A. Cotton and R.A. Walton, Multiple Bonds Between Metal Atoms, Wiley, New York, 1982, pp. 245-264, and references therein.
10 M.H. Chisholm and F.A. Cotton, Acc. Chem. Res., 11 (1978) 356 and references therein.
11 R.J. Klingler, W. Butler and M.D. Curtis, J. Am. Chem. Soc., 97 (1975) 3535.
12 M.D. Curtis and R.J. Klingler, J. Organometal. Chem., 161 (1978) 23.
13 M.D. Curtis, K.R. Han and W.M. Butler, Inorg. Chem., 19 (1980) 2096.
14 M.D. Curtis and W.M. Butler, J. Chem. Soc., Chem. Commun., (1980) 998.
15 L. Messerle and M.D. Curtis, J. Amer. Chem. Soc., 102 (1980) 7789.
16 M.D. Curtis, L. Messerle, N.A. Fotinos and R.F. Gerlach, Adv. Chem. Ser., 155 (1981) 221.
17 D.S. Ginley, C.R. Bock and M.S. Wrighton, Inorg. Chim. Acta, 23 (1977) 85.
18 R.D. Adams, D.A. Katahira and Li–Wu Yang, Organometallics, 1 (1982) 231.
19 M.C. Chisholm, F.A. Cotton, M.W. Extine and L.A. Rankel, J. Am. Chem. Soc., 100 (1978) 807.

20 W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton, C.A. Murillo and L.A. Rankel, J. Amer. Chem. Soc., 100 (1978) 802; W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton and L.A. Rankel, J. Amer. Chem. Soc., 100 (1978) 5764.

21 G.K. Barker, W.E. Carroll, M. Green and A.J. Welch, J. Chem. Soc., Chem. Commun., (1980) 1071.

22 J. Wachter, A. Mitschler and J.G. Riess, J. Amer. Chem. Soc., 103 (1981) 2121.

23 R. Goddard, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 147.

24 S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 173; S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Chem. Commun., (1978) 221.

25 J.A. Beck, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter and P. Woodward, J. Chem. Soc., Dalton Trans., (1982) 195.

26 C.P. Gibson, Jin-Shun Huang and L.F. Dahl, to be published.

27 C.P. Gibson and L.F. Dahl, to be published.

28 R.B. King and M.B. Bisnette, J. Organometal. Chem., (1967) 287.

29 R.B. King and A. Efraty, J. Amer. Chem. Soc., 93 (1971) 4950.

30 R.B. King and A. Efraty, J. Amer. Chem. Soc., 94 (1972) 2773.

31 J. Potenza, P. Giordano, D. Mastropaolo, A. Efraty and R.B. King, J. Chem. Soc., Chem. Commun., (1972) 1333.

32 J. Potenza, P. Giordano, D. Mastropaolo and A. Efraty, Inorg. Chem., 13 (1974) 2540.

33 R.D. Adams, D.E. Collins and F.A. Cotton, J. Amer. Chem. Soc., 96 (1974) 749.

34 F.C. Wilson and D.P. Shoemaker, J. Chem. Phys., 27 (1957) 809.

35 R.D. Adams, D.M. Collins and F.A. Cotton, Inorg. Chem., 13 (1974) 1086.

36 R.C. Job and M.D. Curtis, Inorg. Chem., 12 (1973) 2510.

37 P. Hackett, P.S. O'Neill and A.R. Manning, J. Chem. Soc. Dalton Trans., (1974) 1625.

38 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 4246.

39 R.J. Klingler, W.M. Butler and M.D. Curtis, J. Amer. Chem. Soc., 100 (1978) 5034.

40 M.D. Curtis and W.M. Butler, J. Organometal. Chem., 155 (1978) 131.

41 E.D. Jemmis, A.R. Pinhas and R. Hoffmann, J. Amer. Chem. Soc., 102 (1980) 2576.

42 R. Colton and M.L. McCormick, Coord. Chem. Revs., 31 (1980) 1.

43 R.B. King, M.Z. Iqbal and A.D. King, Jr., J. Organometal. Chem. 171 (1979) 53.

44 L.R. Byers and L.F. Dahl, Inorg. Chem., 19 (1980) 680.

45 F.A. Cotton, W.H. Ilsley and W. Kaim, J. Amer. Chem. Soc., 102 (1980) 1918.

46 F. Huq, W. Mowat, A. Shortland, A.C. Skapski and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1971) 1079.

47 M.H. Chisholm, F.A. Cotton, B.A. Frenz, W.W. Reichert, L.W. Shive and B.R. Stults, J. Amer. Chem. Soc., 98 (1976) 4469.

48 M.H. Chisholm, F.A. Cotton, C.A. Murillo and W.W. Reichert, Inorg. Chem., 16 (1977) 1801.

49 F.A. Cotton, L. Kruczynski and B.A. Frenz, J. Organometal. Chem. 160 (1978) 93.

50 F.A. Cotton, Prog. Inorg. Chem., 21 (1974) 1.

51 C.J. Commons and B.F. Hoskins, Aust. J. Chem., 28 (1975) 1663.

52 R. Colton and C.J. Commons, Aust. J. Chem., 28 (1975) 1673.

53 R. Colton, C.J. Commons and B.F. Hoskins, J. Chem. Soc. Chem. Commun., (1975) 363.

54 A.A. Pasynskii, Yu. V. Skripkin, I.L. Eremenko, V.T. Kalinnikov, G.G. Aleksandrov, V.G. Andrianov and Yu. T. Struchkov, J. Organometal. Chem., 165 (1979) 49.

55 M. Manassero, M. Sansoni and G. Longoni, J. Chem. Soc. Chem. Commun., (1976) 919.

56 W.A. Herrmann, M.L. Ziegler, K. Weidenhammer and H. Biersack, Angew. Chem. Int. Ed. Engl., 18 (1979) 960.

57 W.A. Herrmann, H. Biersack, M.L. Ziegler, K. Weidenhammer, R. Siegel and D. Rehder, J. Amer. Chem. Soc., 103 (1981) 1692.

58 F.A. Cotton and R.A. Walton, Multiple Bonds Between Metal Atoms, Wiley, New York, 1982, pp. 183–264.

59 Trinh-Toan, R.W. Broach, S.A. Gardner, M.D. Rausch and L.F. Dahl, Inorg. Chem., 16 (1977) 279.