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An NMR spectroscopic and EHMO investigation of cationic mixed metal clusters: X-ray crystal structure of (1,7,7-trimethyl-μ^2-2-propynylnorbornene)-bis(cyclopentadienyl)tetracarbonyldimolybdenum *

Michael F. D'Agostino, Christopher S. Frampton and Michael J. McGlinchey *

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1 (Canada)

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Abstract

The reaction of $(C_5H_5)_2Mo_2(CO)_4$ with 2-*endo*-propynylborneol yields the tetrahedral cluster $(R^*C{\equiv}CMe)Mo_2(CO)_4(C_5H_5)_2$ (7), where R^* is the 2-norbornenyl group. This chiral molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with a 8.938(4), b 14.074(4), c 19.510(6) Å, V 2268(1) Å^3, D_c 1.65 g cm^{-3}, D_m 1.64 g cm^{-3}, for $Z = 4$, and $R_1 = 0.0290$ ($R_2 = 0.0276$) for 4350 unique reflections ($R_1 = 0.0236$, $R_2 = 0.0245$ for 3846 reflections with $I > 2.5\sigma(I)$). Protonation of 7 and of the related dicobalt cluster (2-*endo*-propynylborneol)$Co_2(CO)_6$ leads to metal stabilized cations which maintain their terpenoid skeletons and are stable towards carbocationic rearrangement. Protonation of the mixed metal clusters $(C_5H_4Me)W(CO)_2Co(CO)_3(HC{\equiv}CCH_2OH)$, $(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}CCH_2OH)$, and $(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}CHEtOH)$ yields the corresponding cationic clusters $[M{-}Co(CO)_3(HC{\equiv}CCR_2)]^+$. High field NMR spectroscopy reveals that the capping vinylidene moiety leans preferentially towards one vertex and the facile antarafacial migration which is observed in the homometallic complexes $[M{-}M(HC{\equiv}CCH_2)]^+$ ($M = Co(CO)_3$, $(C_5H_5)Mo(CO)_2$ or $(C_5H_5)W(CO)_2$) has a very high barrier in these mixed metal systems. Variable-temperature NMR studies on the mixed trimetallic cluster cation $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3)_2]^+$ confirm that the carbocationic centre is better stabilized on the molybdenum vertex rather than by the tricarbonylcobalt fragment. These results are supplemented by EHMO calculations which demonstrate not only that the positive charge is better tolerated at the $(C_5H_5)Mo(CO)_2$ vertex but also that the transition state for antarafacial migration is strongly disfavored.

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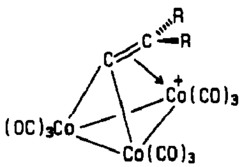
* Dedicated to Prof. F.G.A. Stone on the occasion of his 65th birthday.

Introduction

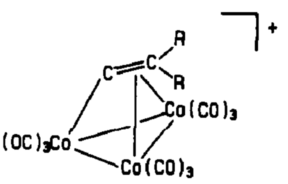
The ability of trimetallic tetrahedral clusters to stabilize a positive charge in the α-position was reported some years ago by Seyferth [1]. With typical insight he proposed that this stabilization could be attributed to delocalization of the charge onto the carbonyl ligands via a direct interaction with a metal centre. This view was reinforced by the EHMO calculations of Schilling and Hoffmann who found that the capping ethylidene group in $[Co_3(CO)_9CCH_2]^+$ is preferentially sited over a metal vertex as in **1a**; it was also reported that structure **1b**, in which the plane of the methylene group bisects a cobalt–cobalt vector, could provide a pathway by which the capping group could migrate around the basal triangle [2].

A subsequent ^{13}C NMR study on the $[Co_3(CO)_9CC(H)CHMe_2]^+$ system by Edidin, Norton and Mislow [3] provided experimental confirmation of the Schilling–Hoffmann model. When the $C{=}CR_2$ moiety is vertical, as in **1c**, the methyls in the isopropyl substituent are magnetically equivalent; in **1a**, however, these methyls should be diastereotopic and the ^{13}C NMR peak is indeed split at low temperature [3]. Analogously, EHMO calculations and ^{13}C NMR data on the ketenylidene cluster $[Co_3(CO)_9C{=}C{=}O]^+$ (**2**) also suggest that the positive charge is delocalized onto a metal vertex [4].

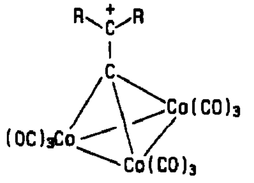
Isolobal replacement of a $Co(CO)_3$ vertex in **1** by a carbynyl ($RC{\equiv}$) moiety leads to $[Co_2(CO)_6(RC{\equiv}CCR_2)]^+$ cationic clusters whose chemistry has been profitably exploited in recent years [5]. The evidence accumulated thus far indicates that the alkylidene group readily migrates between the two cobalt vertices in **3a** or between the two molybdenum vertices in **3b** [6,7]. To assess the relative charge-stabilizing capabilities of different organometallic fragments, we have synthesized a variety of hetero-bimetallic cationic clusters and now describe their variable-temperature NMR spectra.



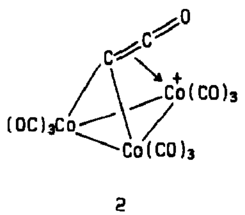
1a



1b



1c



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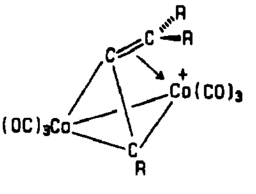
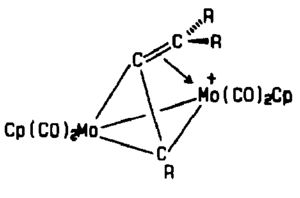


3a



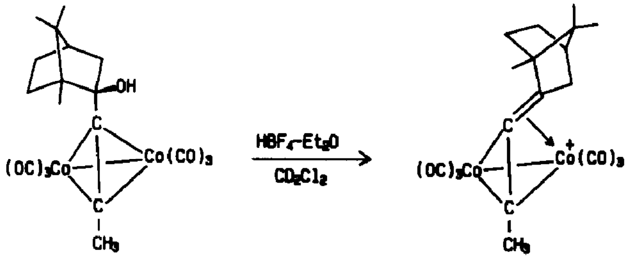
3b

Results and discussion

We have recently reported the synthesis and X-ray crystal structure of the chiral (μ-alkyne)$Co_2(CO)_6$ complex **4** which bears the natural product borneol as a substituent [8]. Subsequently, in an attempt to obtain the analogous (μ-alkyne)$Mo_2(CO)_4Cp_2$ complex (**6**), a product was isolated which the NMR and mass spectroscopic data indicated to be the alkene cluster **7**. A plausible route to this latter complex involves protonation of the hydroxyl function of **6**, loss of water to yield the cation **8**, and finally deprotonation to give the alkene **7**. The presumed intermediacy of the metal-stabilized cation raises two key questions: (i) can one isolate the cations **5** and **8** by protonation of **4** and **7**, respectively? (ii) are the cations stable or do they undergo skeletal rearrangement as is common in terpenoid systems [9]? In connection with this latter point we learned that low temperature protonation of the steroidal complex **9** [10] yields the cation **10** which undergoes methyl group migration at ambient temperature [11].

The dimolybdenum complex **7** crystallizes as purple-black prisms suitable for an X-ray diffraction study. Figure 1 shows a view of the molecule and reveals that the original borneol moiety has indeed been dehydrated across the C(2)–C(3) bond, as indicated from the spectroscopic data. Unlike the dicobalt complex **4**, in which the tetrahedral nature of the C(2) centre brings about some degree of steric crowding at one of the $Co(CO)_3$ vertices, the two dicarbonyl(cyclopentadienyl)molybdenum fragments are relatively unencumbered by the chiral organic group.

The sp^2 character of C(2) in **7** leaves the tetrahedral cluster splayed away from the terpene and the basic Mo_2C_2 framework adopts the tetrahedral geometry so typical of these molecules [12–14]. The Mo–Mo bond length of 2.972(1) Å is in the normal range for these systems. The crystallographic data including all the im-



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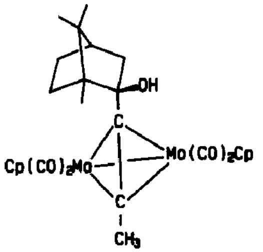

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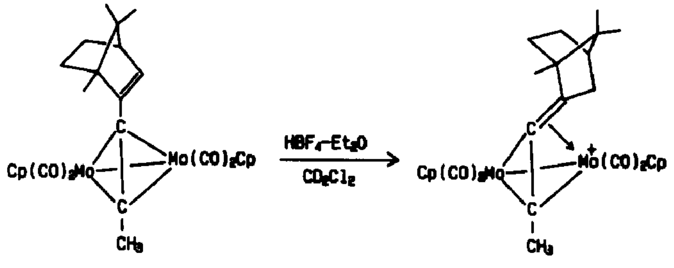
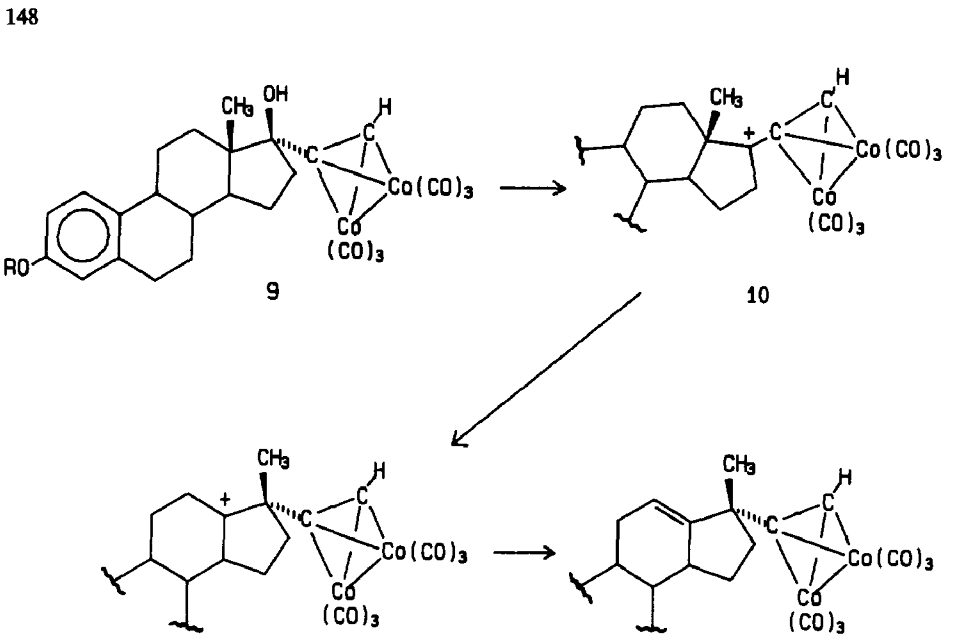


7

8



portant bond lengths and angles are collected in Tables 1 through 3. The fold angles of the cluster, i.e., the interplane angles between C(11)–C(12)–Mo(1) and C(11)–C(12)–Mo(2) and between C(11)–Mo(1)–Mo(2) and C(12)–Mo(1)–Mo(2) are 90 and 131°, respectively. A characteristic feature of many of these (μ^2-alkyne)$Mo_2(CO)_4Cp_2$ clusters is the asymmetric nature of the tetrahedral unit. As was first pointed out by Cotton [12], the two cyclopentadienyl rings are oriented so as to generate a system with almost C_2 symmetry; moreover, the chiral nature of the

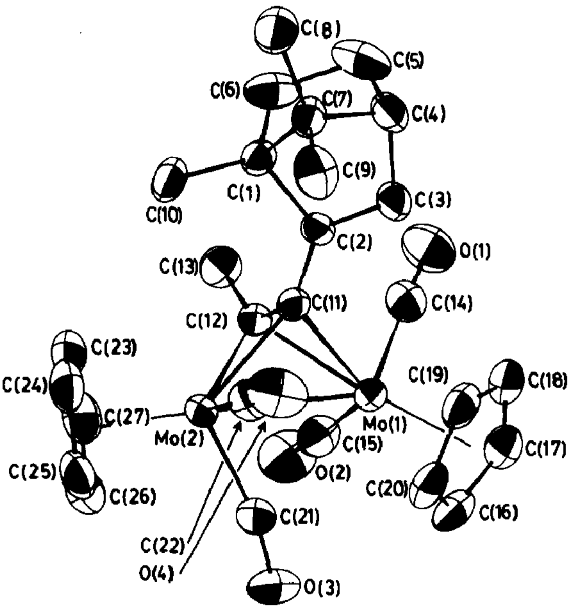


Fig. 1. View of (1,7,7-trimethyl-μ^2-2-propynylnorbornene)bis(cyclopentadienyl)tetracarbonyldimolybdenum (7).

Table 1

Crystal data for $[(Mo(C_5H_5)(CO)_2)_2(C_{13}H_{18})]$

Formula	$C_{27}H_{28}Mo_2O_4$
f.w.	608.40
System	Orthorhombic
Systematic absences	$h00$, $h \neq 2n$, $0k0$, $k \neq 2n$, $00l$, $l \neq 2n$
Space group	$P2_12_12_1$, No. 19
a, Å	8.938(4)
b, Å	14.074(4)
c, Å	19.510(6)
V, Å^3	2454(1)
Z	4
D_c, g cm^{-3}	1.65
D_m, g cm^{-3}	1.64
$F(000)$	1209.76(1224)
μ(Mo-K_α), cm^{-1}	10.36
Final R_1, R_2 ^{a,d}	0.0290, 0.0276
Weighting scheme	$w = (\sigma^2 F + 0.000342 F^2)^{-1}$
Error in observation of unit weight ^{b}	1.0881
Highest peak, eÅ^{-3}; location	0.55; 0.6776, −0.0217, 0.7422 ^{c}
Lowest peak, eÅ^{-3}	−0.53

^{a} $R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$; $R_2 = (\Sigma w(| F_o | - | F_c |)^2 / \Sigma w F_o^2)^{1/2}$. ^{b} $S = (\Sigma w(| F_o | - | F_c |)^2/(m - n))^{1/2}$, m = no. of reflections, n = no. of variables. ^{c} 0.80 Å from H(19). ^{d} R and R_2 for 3846 reflections with $I > 2.58\sigma(I)$ 0.0236 and 0.0245, respectively.

tetrahedral framework is accentuated by the presence of a semi-bridging carbonyl ligand. This asymmetry is also observed in cluster 7; the cyclopentadienyl rings are twisted so as to make a Cp(centroid)–Mo–Mo–Cp(centroid) dihedral angle of 143°. As expected, one of the carbonyls is in a semibridging position; the Mo(2)–C(21)–O(3) angle is 167° while the corresponding angles for the terminal Mo-CO ligands are ≈ 178°. Cotton also demonstrated [12] that two fluxional processes are detectable in these systems: the first involves an exchange of terminal and semi-bridging carbonyls while the second process equilibrates the environments of the cyclopentadienyl units. In the present molecule, the chiral nature of the terpene group renders all four carbonyls magnetically non-equivalent even at room temperature and so, at low temperatures when these fluxional processes are slow on the NMR time scale, one can detect diastereomers produced by semi-bridging carbonyls in different positions. A full discussion of the variable-temperature NMR spectra of 7 and related molecules is deferred to another paper [15].

Protonation studies

Upon protonation of a CD_2Cl_2 solution of either 4 or 7 in an NMR tube with HBF_4-Et_2O at approximately −40 °C, an immediate colour change to a deeper red was observed. In each case, the ^1H and ^{13}C NMR spectra of the cations at −40 °C were readily interpretable in terms of a single unrearranged species. These spectra were assigned by using conventional one- and two-dimensional techniques, viz., 500 MHz ^1H–^1H COSY and ^1H–^{13}C shift-correlated experiments. Upon raising the temperature to +20 °C no noticeable spectral changes were observable; apparently, the presence of either a dicobalt or dimolybdenum tetrahedral cluster in a position α

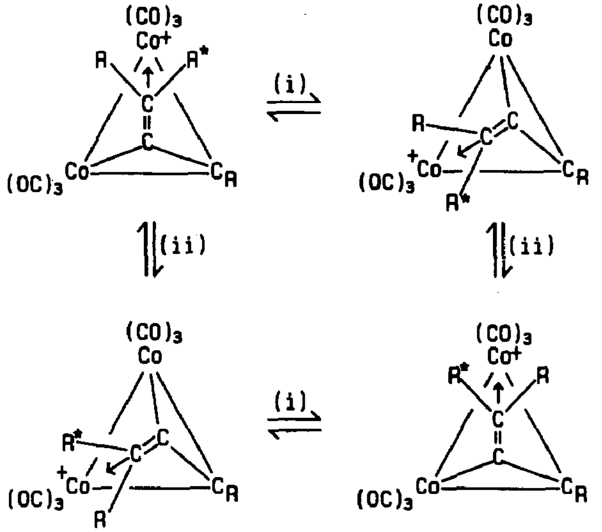
Table 2

Positional parameters ($\times 10^4$) and U_{eq} (Å^2, $\times 10^4$) for $[(Mo(C_5H_5)(CO)_2)_2(C_{13}H_{18})]$ with estimated standard deviations in parentheses

Atom	x	y	z	U_{eq} [a]
Mo(1)	3192.7(3)	-126.4(2)	7477.2(2)	313
Mo(2)	2467.8(4)	1430.7(2)	6503.5(1)	328
C(1)	4694(4)	−512(3)	5158(2)	353
C(2)	4727(4)	−467(2)	5950(2)	312
C(3)	5796(5)	−1063(3)	6148(2)	427
C(4)	6458(5)	−1532(3)	5522(2)	465
C(5)	5204(6)	−2207(3)	5266(3)	650
C(6)	4003(5)	−1505(3)	5017(2)	565
C(7)	6378(4)	−712(3)	5002(2)	392
C(8)	6696(5)	−1016(4)	4257(2)	601
C(9)	7411(6)	101(3)	5167(2)	566
C(10)	3985(5)	309(3)	4778(2)	497
C(11)	3608(4)	5(3)	6377(2)	313
C(12)	2095(4)	−61(2)	6449(2)	334
C(13)	867(5)	−654(3)	6142(2)	450
C(14)	2760(5)	−1489(3)	7292(2)	455
O(1)	2521(6)	−2270(2)	7205(2)	754
C(15)	1038(5)	−83(3)	7710(2)	484
O(2)	−231(4)	−84(3)	7819(2)	748
C(16)	4060(5)	400(3)	8536(2)	524
C(17)	4230(6)	−599(3)	8506(2)	545
C(18)	5307(6)	−784(4)	7986(2)	573
C(19)	5807(5)	74(4)	7713(2)	524
C(20)	5054(5)	814(3)	8050(2)	525
C(21)	2473(5)	1819(2)	7456(2)	450
O(3)	2338(5)	2212(2)	7986(2)	707
C(22)	4603(5)	1679(3)	6415(2)	451
O(4)	5864(4)	1837(3)	6348(2)	711
C(23)	817(6)	1602(3)	5560(3)	575
C(24)	1866(6)	2325(3)	5539(2)	610
C(25)	1628(6)	2911(3)	6138(3)	703
C(26)	429(6)	2515(4)	6491(3)	702
C(27)	−61(6)	1704(4)	6144(3)	655

[a] $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

to the cationic site successfully stabilizes the terpene moiety against structural rearrangement. Furthermore, when a cooled CD_2Cl_2 solution of the dicobalt cation **5** was treated with H_2O and allowed to warm gradually to room temperature the product was shown by ^{13}C NMR spectroscopy to be not the original alcohol **4** but rather the dicobalt alkene cluster analogous to **7**. These observations support the proposal that the cation **8** acts as an intermediate in the dehydration of the hydroxylated cluster **7**. Such a picture can also account for an observation of Seyferth who described the generation of $Co_3(CO)_9CCMe_2OMe$ from $[(OC)_9Co_3CCMe_2]^+PF_6^-$ and MeOH. It was found that the product obtained was critically dependent on the work-up procedure. Sublimation of the crude product mixture gave the desired product, whereas column chromatography on silicic acid yielded the alcohol $Co_3(CO)_9CCMe_2OH$ [16]. It would appear either that, under acidic



Scheme 1. The fluxional processes occurring in $[Co_2(CO)_6(HC{\equiv}CRR^*)]^+$ systems: (i) antarafacial migration resulting in racemization of the complex; (ii) interconversion of diastereomers, presumably via an upright cationic centre as in 1c. (In this scheme, R* is not a chiral group.)

conditions, the ether cluster gave rise to the metal-stabilized cation which subsequently reacted with traces of water to give the alcohol.

NMR observations on dimetalla-tetrahedrane cluster cations have been previously reported by a number of groups. Nicholas has shown [17] that the methyl groups in $[Co_2(CO)_6(HC{\equiv}CCMe_2)]^+$ are non-equivalent at low temperature; this supports the idea that the positive charge is not sited merely on an upright α-carbon but rather is delocalized via a direct bonding interaction with a cobalt vertex. This work has been elegantly extended by Schreiber [6] who established the existence of two fluxional processes, as depicted in Scheme 1: (i) a low energy ($\approx$ 10 kcal mol^{-1}) antarafacial migration of an alkylidene moiety from one $Co(CO)_3$ to the other, entirely analogous to the known behaviour of $[Co_3(CO)_9CC(H)\overset{+}{C}HMe_2]^+$ [3]; (ii) a higher energy process ($\approx$ 13 kcal mol^{-1}) which equilibrates *syn* and *anti* isomers, probably via an upright carbocationic structure. This latter proposal is in accord with the observation that the activation energy barrier for this second fluxional process is lower for 3° than for 2° cations; one might reasonably suppose that the more stable carbocation, viz. the 3° system, has less need for anchimeric assistance from a metal than does the 2° carbocation.

Furthermore, following earlier NMR reports by Russian workers [18], Curtis [7], Green [19], and more recently Jaouen [11] have obtained X-ray crystallographic evidence of the interaction of the carbocationic center with a $(C_5H_5)M(CO)_2$ vertex, where M = Mo or W. Again, these molecules exhibit fluxional behaviour whereby the $C{=}CR_2$ fragment can migrate from tungsten to tungsten (presumably via both of the above-mentioned processes) with an activation energy barrier of approximately 10 kcal mol^{-1}. Interestingly, in the $[(C_5H_4Me)_2Mo_2(CO)_4(HC{\equiv}CCH_2)]^+$ system studied by Curtis [7] the activation energy for migration of the $C{=}CH_2$ moiety from molybdenum to molybdenum (which is detectable as an equilibration of the methylcyclopentadienyl environments) is noticeably higher ($\approx$ 17 kcal mol^{-1}) than for the corresponding $C{=}CMe_2$ exchange between tungsten sites. Moreover, the

Table 3

Selected bond lengths (Å) and angles (°) for [(Mo(C$_5$H$_5$)(CO)$_2$)$_2$(C$_{13}$H$_{18}$)], with estimated standard deviations in parentheses

(i) *Molybdenum coordination*			
Mo(1)–Mo(2)	2.972(1)		
Mo(1)–C(11)	2.187(3)	Mo(2)–C(11)	2.265(4)
Mo(1)–C(12)	2.236(3)	Mo(2)–C(12)	2.129(3)
Mo(1)–C(14)	1.990(4)	Mo(2)–C(21)	1.937(4)
Mo(1)–C(15)	1.980(4)	Mo(2)–C(22)	1.948(4)
Mo(1)–C(16)	2.328(4)	Mo(2)–C(23)	2.371(4)
Mo(1)–C(17)	2.308(4)	Mo(2)–C(24)	2.328(4)
Mo(1)–C(18)	2.327(4)	Mo(2)–C(25)	2.327(4)
Mo(1)–C(19)	2.399(4)	Mo(2)–C(26)	2.377(5)
Mo(1)–C(20)	2.403(4)	Mo(2)–C(27)	2.398(5)
Mo(1)–Ctd(1)[†]	2.017	Mo(2)–Ctd(2)	2.036
C(11)–Mo(1)–C(12)	35.9(1)	C(11)–Mo(2)–C(12)	36.0(1)
C(11)–Mo(1)–C(14)	86.3(1)	C(11)–Mo(2)–C(21)	110.7(1)
C(11)–Mo(1)–C(15)	112.8(1)	C(11)–Mo(2)–C(22)	73.0(1)
C(12)–Mo(1)–C(14)	77.9(1)	C(12)–Mo(2)–C(21)	109.1(1)
C(12)–Mo(1)–C(15)	77.2(1)	C(12)–Mo(2)–C(22)	109.0(1)
C(14)–Mo(1)–C(15)	83.2(2)	C(21)–Mo(2)–C(22)	91.8(2)
Mo(1)–C(11)–Mo(2)	83.7(1)	Mo(1)–C(12)–Mo(2)	85.8(1)
Mo(1)–C(11)–C(2)	129.6(2)	Mo(2)–C(11)–C(2)	140.6(2)
Mo(1)–C(11)–C(12)	74.0(2)	Mo(2)–C(11)–C(12)	66.6(2)
Mo(1)–C(12)–C(11)	70.1(2)	Mo(2)–C(12)–C(11)	77.4(2)
Mo(1)–C(12)–C(13)	131.0(3)	Mo(2)–C(12)–C(13)	132.9(3)
C(11)–Mo(1)–Mo(2)	49.2(1)	C(11)–Mo(2)–Mo(1)	47.0(1)
C(12)–Mo(1)–Mo(2)	45.5(1)	C(12)–Mo(2)–Mo(1)	48.6(1)
C(14)–Mo(1)–Mo(2)	123.5(1)	C(21)–Mo(2)–Mo(1)	66.1(1)
C(15)–Mo(1)–Mo(2)	85.0(1)	C(22)–Mo(2)–Mo(1)	88.6(1)
C(16)–Mo(1)–Mo(2)	113.9(1)	C(23)–Mo(2)–Mo(1)	135.0(1)
C(17)–Mo(1)–Mo(2)	148.9(1)	C(24)–Mo(2)–Mo(1)	165.1(1)
C(18)–Mo(1)–Mo(2)	138.0(1)	C(25)–Mo(2)–Mo(1)	157.9(2)
C(19)–Mo(1)–Mo(2)	104.3(1)	C(26)–Mo(2)–Mo(1)	130.3(2)
C(20)–Mo(1)–Mo(2)	92.4(1)	C(27)–Mo(2)–Mo(1)	120.7(1)
Ctd(1)–Mo(1)–C(11)	120.5	Ctd(2)–Mo(2)–C(11)	136.5
Ctd(1)–Mo(1)–C(12)	156.0	Ctd(2)–Mo(2)–C(12)	113.7
Ctd(1)–Mo(1)–C(14)	109.7	Ctd(2)–Mo(2)–C(21)	109.6
Ctd(1)–Mo(1)–C(15)	125.5	Ctd(2)–Mo(2)–C(22)	121.1
(ii) *1,7,7-Trimethyl-2-propynylnorbornene*			
C(2)–C(3)	1.329(5)	C(1)–C(6)	1.553(6)
C(1)–C(2)	1.546(5)	C(1)–C(10)	1.513(6)
C(2)–C(11)	1.461(5)	C(1)–C(7)	1.561(5)
C(3)–C(4)	1.509(5)	C(7)–C(9)	1.505(6)
C(4)–C(5)	1.552(6)	C(7)–C(8)	1.542(5)
C(4)–C(7)	1.539(5)	C(11)–C(12)	1.363(5)
C(5)–C(6)	1.537(7)	C(12)–C(13)	1.502(5)
C(1)–C(2)–C(3)	106.1(3)	C(2)–C(1)–C(7)	100.6(3)
C(11)–C(2)–C(3)	127.8(3)	C(6)–C(1)–C(7)	100.8(3)
C(11)–C(2)–C(1)	125.1(3)	C(10)–C(1)–C(7)	116.4(3)
C(2)–C(3)–C(4)	108.8(3)	C(4)–C(7)–C(1)	92.9(3)
C(3)–C(4)–C(5)	104.1(3)	C(4)–C(7)–C(9)	113.6(3)
C(3)–C(4)–C(7)	100.8(3)	C(1)–C(7)–C(9)	114.4(3)

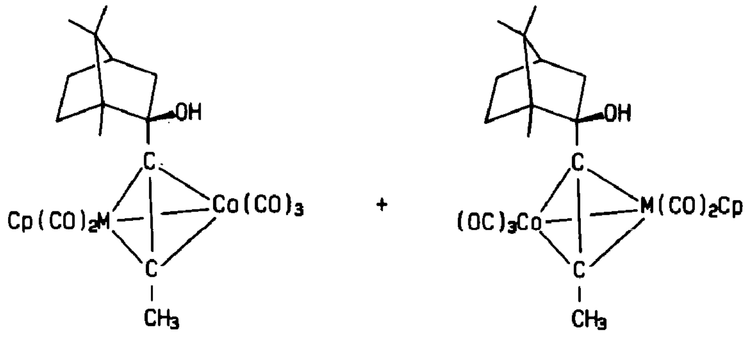
Table 3 (continued)

(ii) *1,7,7-Trimethyl-2-propynylnorbornene*			
C(5)–C(4)–C(7)	102.3(3)	C(4)–C(7)–C(8)	113.8(3)
C(4)–C(5)–C(6)	102.3(3)	C(1)–C(7)–C(8)	114.4(3)
C(5)–C(6)–C(1)	104.1(4)	C(9)–C(7)–C(8)	107.5(4)
C(6)–C(1)–C(2)	102.8(3)	C(2)–C(11)–C(12)	134.9(3)
C(6)–C(1)–C(10)	115.7(3)	C(11)–C(12)–C(13)	136.2(3)
C(2)–C(1)–C(10)	117.8(3)		
(iii) *Carbonyls and cyclopentadienyls*			
C(14)–O(1)	1.133(5)	C(21)–O(3)	1.179(5)
C(15)–O(2)	1.154(5)	C(22)–O(4)	1.57(5)
Mo(1)–C(14)–O(1)	178.1(4)	Mo(2)–C(21)–O(3)	166.8(3)
Mo(1)–C(15)–O(2)	176.8(4)	Mo(2)–C(22)–O(4)	178.4(4)
C(16)–C(17)	1.417(6)	C(23)–C(24)	1.385(7)
C(17)–C(18)	1.421(6)	C(24)–C(25)	1.445(7)
C(18)–C(19)	1.395(7)	C(25)–C(26)	1.390(8)
C(19)–C(20)	1.404(6)	C(26)–C(27)	1.397(7)
C(16)–C(20)	1.423(6)	C(23)–C(27)	1.391(7)
C(20)–C(16)–C(17)	108.2(4)	C(27)–C(23)–C(24)	109.3(4)
C(16)–C(17)–C(18)	106.5(4)	C(23)–C(24)–C(25)	107.2(5)
C(17)–C(18)–C(19)	109.4(4)	C(24)–C(25)–C(26)	106.6(5)
C(18)–C(19)–C(20)	108.0(4)	C(25)–C(26)–C(27)	109.3(5)
C(19)–C(20)–C(16)	108.0(4)	C(26)–C(27)–C(23)	107.6(5)

[a] Ctd(1) and Ctd(2) are the calculated centroids of the two cyclopentadienyl rings.

higher energy process which exchanges the two methylene proton signals and requires an upright carbocation is not observed for this primary ($-CH_2^+$) species; this result is in accord with Schreiber's proposal [6] outlined above.

These published reports on homo-bimetallic species, together with our own observations on the behaviour of the dicobalt and dimolybdenum cluster cations 5



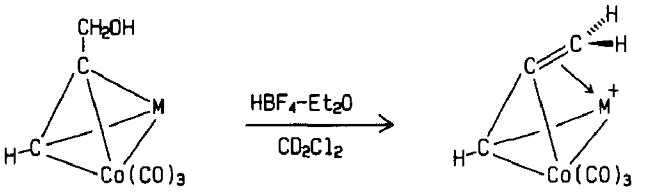
11 M = Mo

12 M = W

and **8** led us to consider which organometallic fragment, namely $Co(CO)_3$ or $(C_5H_5)M(CO)_2$, where M = Mo or W, was better able to stabilize a positive charge in the α position.

Although we had described the syntheses of the hetero-bimetallic analogues, **11** and **12**, of the dicobalt borneol cluster **5** in which both a $Co(CO)_3$ and a $(C_5H_5)M(CO)_2$ (M = Mo, W) vertex were present [8], the complexity of the spectra associated with these systems would undoubtedly have proven overwhelming if we had tried to carry out a competitive protonation study on them. Instead we chose to examine some simpler propargyl alcohol derivatives of heterobimetallic clusters.

We have previously reported that treatment of (propargyl alcohol)$Co_2(CO)_6$ with $(C_5H_5)Mo(CO)_3^-$ or with $(C_5H_4Me)W(CO)_3^-$ yields the chiral hetero-bimetallic clusters $[Co(CO)_3M]$ (μ^2-$HC{\equiv}CCH_2OH$), where M = $(C_5H_5)Mo(CO)_2$ (**13**) or M = $(C_5H_4Me)W(CO)_2$ (**14**) [8]. Treatment of a CD_2Cl_2 solution of the alcohols **13** or **14** in an NMR tube with HBF_4–Et_2O generates the cations $[(HC{\equiv}CCH_2)Co(CO)_3M]^+$ **15** and **16**, respectively.



13 M = $(C_5H_5)Mo(CO)_2$ 15 M = $(C_5H_5)Mo(CO)_2$

14 M = $(C_5H_4Me)W(CO)_2$ 16 M = $(C_5H_4Me)W(CO)_2$

Let us begin with a simple system and see what information we can extract from its NMR behaviour. The cation $[(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}CCH_2)]^+$ (**15**) yields a ^1H NMR spectrum consisting of four resonances in the ratio 5 : 1 : 1 : 1. The same pattern is observed over the entire range of temperatures from +30 °C down to −90 °C. Clearly then the methylene hydrogens are magnetically non-equivalent in this cation and do not interconvert on the NMR timescale. This means that the CH_2^+ group is not a vertically oriented, freely spinning substituent. (Had this been the case, the methylene protons would resonate at the same frequency.) Instead, the vinylidene unit must be leaning or bent over towards the Co–Mo–C triangular base to generate a cluster of C_1 symmetry. In accord with this view, the ^{13}C NMR spectrum of **15** exhibits a single cyclopentadienyl signal, two separate molybdenum carbonyl resonances, a single tricarbonylcobalt peak and also three signals attributable to C, CH and CH_2 environments. Analogously, in $[(C_5H_4Me)W(CO)_2Co(CO)_3$-$(HC{\equiv}CCH_2)]^+$ (**16**) similar peak patterns are observed over the range of temperatures from −80 °C up to ambient temperature except that, instead of the single cyclopentadienyl resonance, the methylcyclopentadienyl ring system gives rise to a CH_3 and four different CH signals in both the ^1H and ^{13}C NMR spectra. These resonances were all assigned by using a combination of 1D and 2D NMR techniques.

The reaction of $(C_5H_5)W(CO)_3^-$ with $Co_2(CO)_6[HC{\equiv}CCH(OH)Et]$ yields $(C_5H_5)W(CO)_2Co(CO)_3[HC{\equiv}CCH(OH)Et]$ (**17**) which exists in two diastereomeric forms (65 : 35). The isomers of **17** are separable and the major diastereomer was protonated at −40 °C to minimize the possibility of proton elimination from the

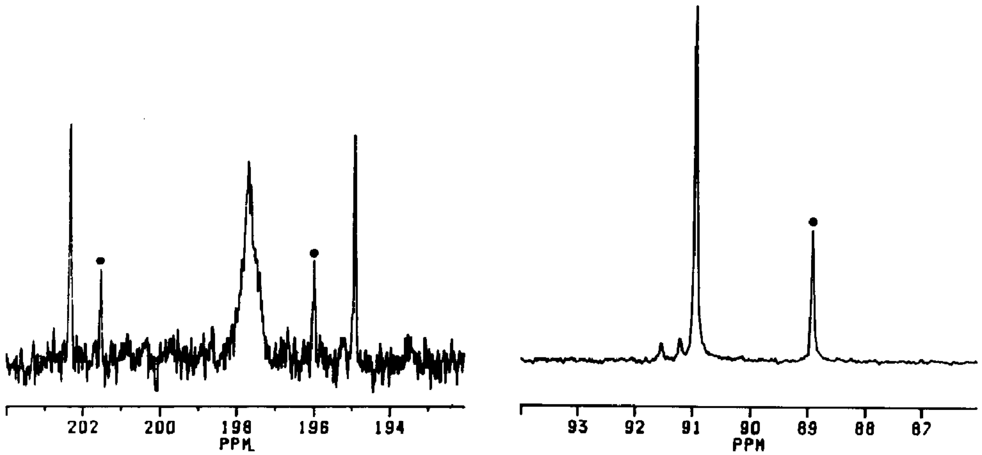
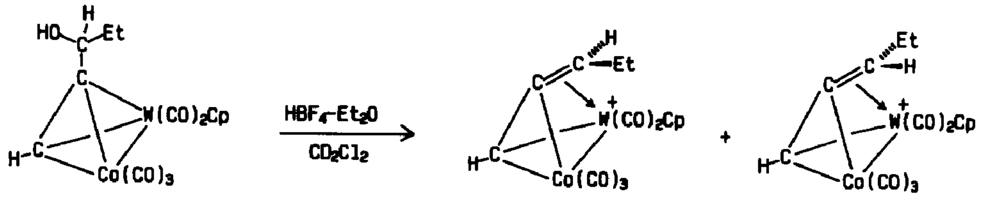


Fig. 2. Section of the 125 MHz ^{13}C NMR spectrum of the diastereomers of $[(C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}CCHEt)]^+$ (**18**) showing two cyclopentadienyl resonances, two pairs of tungsten carbonyl peaks and a broad $Co(CO)_3$ absorption. The peaks for the minor diastereomer are each marked with a dot.

cation to give the corresponding alkene $(C_5H_5)W(CO)_2Co(CO)_3[HC{\equiv}CCH{=}CHMe]$. As shown in Fig. 2, the ^{13}C NMR spectra of the resulting product, $[(C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}CCHEt)]^+$ (**18**), reveal that the protonation of a single diastereomer of **17** yielded two cations in the ratio of approximately 2 : 1. These cations were not interconvertible on the NMR time scale.

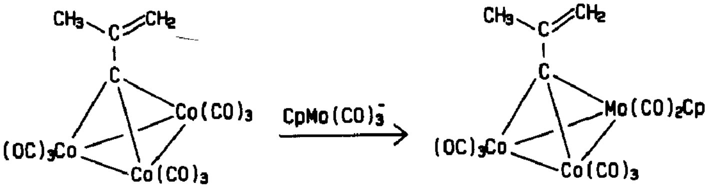


17

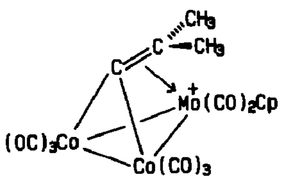
18

We have pointed out already that antarafacial migrations of vinylidene fragments from Co to Co or from W to W have barriers of ≈ 10 kcal mol^{-1}. In all of the Mo–Co or W–Co cationic species described herein there is no evidence for a fluxional process which stops at low temperature. It is difficult to envisage an exchange process between the two metal sites with a barrier too low to be detected even when using an 11.7 tesla instrument (500 MHz for ^1H; 125 MHz for ^{13}C). In particular, if migration between cobalt and molybdenum (tungsten) were occurring, one would have expected to freeze out two chemically distinct C_5H_5 environments in the ^{13}C NMR spectrum at low temperature; typically, in $[(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}CCH_2)]^+$ (**15**) we see a single sharp cyclopentadienyl resonance at all temperatures.

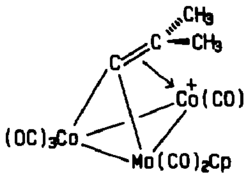
The most straightforward explanation for these observations is that the C=CR′R″ moiety lies above and is directly bonded to only one of the metal vertices—probably the $CpM(CO)_2$ vertex. Thus the NMR spectra of $[(C_5H_5)Mo(CO)_2Co(CO)_3(HC{\equiv}CCH_2)]^+$ (**15**) and of $[(C_5H_4Me)W(CO)_2Co(CO)_3(HC{\equiv}CCH_2)]^+$ (**16**) reveal in each case a single species in which one of the methylene hydrogens is *syn* to the



20 21



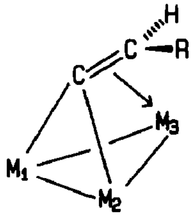
19a



19b

alkyne CH group while the other is *anti*. Similarly, in $[(C_5H_5)W(CO)_2Co(CO)_3(HC{\equiv}CCHEt)]^+$ (**18**) the diastereomers differ in that the ethyl substituent can be either *syn* or *anti* to the alkyne CH unit. We note particularly the large chemical shift difference between the ^{13}C resonances of the $CH_3\mathit{C}H_2$ substituents in the *syn* and *anti* isomers; certainly, these methylene carbon nuclei could be in very different environments relative to the anisotropic shielding cones associated with the cyclopentadienyl groups [20]. The ready isolation and crystallographic characterization of Mo- and W-stabilized cations suggests that the vinylidene moiety is localized on the Group VI vertex rather than on the $Co(CO)_3$ unit. To assess the viability of this hypothesis, we synthesized the trimetallic cation $[(C_5H_5)Mo(CO)_2Co_2(CO)_6$-$CCMe_2]^+$ (**19**), in which an isolobal replacement of CH by $Co(CO)_3$ has been realized. To this end, we used the procedure described by Seyferth to prepare the alkene cluster $Co_3(CO)_9CC(Me){=}CH_2$ (**20**); vertex replacement of a $Co(CO)_3$ fragment by the isolobal $(C_5H_5)Mo(CO)_2$ group yielded **21** and subsequent protonation of the capping $-CMe{=}CH_2$ moiety led to the desired isopropyl cation (**19**).

It is relevant to mention that, although the present work describes cationic clusters with capping vinylidene groups, there are crystallographically characterized neutral clusters which have the same overall electron count. In $[(C_5H_5)_2W_2(CO)_4Fe(CO)_3C{=}CH_2]$ (**22**) and in $[Co_2(CO)_6Ru(CO)_3C{=}CH^tBu]$ (**23**) the vinylidene leans towards the $Fe(CO)_3$ or $Ru(CO)_3$ vertex, respectively [21,22]. One can thus formally assign an eighteen electron configuration to all three metal atoms in each cluster. Had the vinylidene moiety leant towards a $(C_5H_5)W(CO)_2$ in **22** or a $Co(CO)_3$ vertex in **23** it would have been necessary to write formally zwitterionic structures, as in **24**. In such cases the system frequently tries to address the electronic imbalance via a semi-bridging carbonyl interaction, as in **25** [23]. In the cation **19**, there is no obvious a priori reason for preferentially localizing the charge on a $(C_5H_5)Mo(CO)_2$ rather than a $Co(CO)_3$ vertex and so, in principle, **19a** and **19b** are both viable isomers.

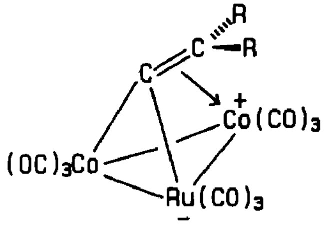


22 $M_1 = M_2 = CpW(CO)_2$

$M_3 = Fe(CO)_3$; R = H

23 $M_1 = M_2 = Co(CO)_3$

$M_3 = Ru(CO)_3$; R = tBu



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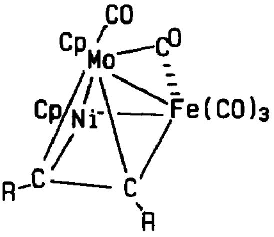

25

Now if we make the reasonable assumption that (at 5.9 tesla) any vinylidene migration process would be slow on the NMR time scale at low temperature, it should be possible to differentiate between **19a** and **19b** (or a mixture of both) simply on the basis of molecular symmetry. In **19a** the cluster has C_s symmetry and the two methyls would remain degenerate; in **19b** the chiral nature of the cluster would render these nuclei magnetically non-equivalent. The experimental result is rather clearcut: the methyl groups maintain their sharp ^{13}C singlet character over the temperature range 0 to −90 °C. One must thus conclude that the vinylidene group remains firmly attached to the molybdenum vertex.

It is noteworthy that in $[Co_3(CO)_9CCMe_2]^+$, which is well established to adopt a bent structure, the ^{13}C NMR spectra of the carbonyl ligands exhibit a 6 : 3 pattern at low temperature. This observation is in accord with the ^{13}CO data on $[Co_3(CO)_9CC{=}O]^+$ which also yields a 6 : 3 pattern at 163 K [4].

EHMO calculations

In light of these observations, we sought an orbital explanation for the marked preference of the vinylidene group to lean towards the molybdenum rather than remain upright or bend towards (or between) the $Co(CO)_3$ vertices. To complement our experimental data on cluster cations, we have carried out molecular orbital calculations at the extended Hückel level. As was first shown by Schilling and Hoffmann [2], $[Co_3(CO)_9C{=}CH_2]^+$ can be constructed conceptually from a tricobalt nonacarbonyl fragment, represented formally as $[Co_3(CO)_9]^{3+}$, and a vinylidene moiety, $[C{=}CH_2]^{2-}$. The former presents a set of three orbitals ($2a_1 + 2e$) well oriented for interaction with a capping unit. Below them lies another set of three frontier orbitals ($1a_1 + 1e$). There is a strong stabilizing interaction of the vinylidene

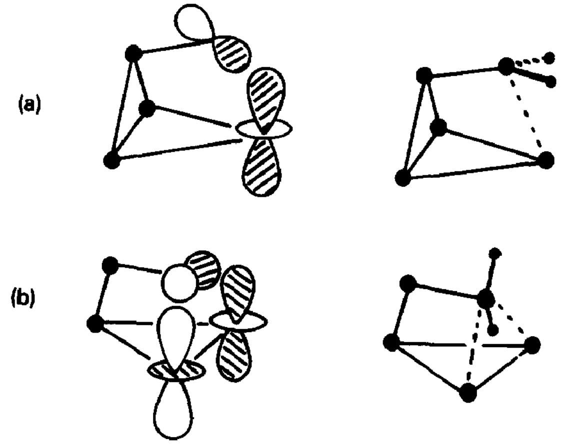

Fig. 3. The interaction of the methylene p orbital with cobalt d_{z^2} orbital(s) in $[Co_3(CO)_9CCH_2]^+$ (A) when the vinylidene fragment is bonded to a single $Co(CO)_3$ centre and the molecular mirror plane bisects the CH_2 unit and (B) when the CH_2 moiety is migrating from one cobalt vertex to another.

lone pair with the vacant $2a_1$ frontier orbital of the metal system. However, the relatively low energy of the π^* orbital of the vinylidene fragment produces a rather low-lying LUMO. Overall this yields a small HOMO–LUMO gap which leaves open the possibility of geometric deformation to stabilize the system. When the vinylidene cap bends towards a cobalt atom, there is a very favorable interaction between the symmetrical component of the $2e$ set of the metal triangle and the π orbital of the $C{=}CH_2$ unit. This latter orbital is well-localized on the methylene carbon and creates direct bonding between this carbon and a cobalt atom (see Fig. 3a); as a result, the HOMO–LUMO gap increases markedly on bending the $C{=}CH_2$ moiety towards a $Co(CO)_3$ vertex.

In our earlier studies on *closo* and *nido* complexes of alkynes with trimetallic fragments [24], we described how the doubly degenerate frontier orbitals of the M_3 moiety are split when one of the $Co(CO)_3$ units is replaced by an isolobal fragment such as $(C_5H_5)Mo(CO)_2$. As shown in fig. 4, the $4s$ orbital is still capable of accepting the vinylidene lone pair in either the upright or bent mode. An important new factor which differentiates the $[(C_5H_5)Mo(CO)_2Co_2(CO)_6]^{3+}$ fragment from the $[Co_3(CO)_9]^{3+}$ triangle previously discussed is the very localized nature of the $3s$ orbital on Mo (40 vs. 4% for the Co atoms).

Figure 5 shows the effect of tilting the $C{=}CH_2$ capping group towards either a $Co(CO)_3$ or a $(C_5H_5)Mo(CO)_2$ vertex. The preference for bonding to the molybdenum rather than to a cobalt atom is augmented if the entire $(C_5H_5)Mo(CO)_2$ fragment is allowed to swivel 10° downwards away from the approaching vinylidene group. This has the effect of minimizing unfavorable steric interactions with the molybdenum carbonyls and concomitantly increasing the HOMO–LUMO gap. Schilling and Hoffmann noted that antarafacial migration of the $C{=}CH_2$ cap in $[Co_3(CO)_9CCH_2]^+$ is facilitated by an interaction between the antisymmetric component of the tricobalt $2e$ set with the π orbital of the vinylidene group, as shown in Fig. 3b. In contrast, we can see from Fig. 5 that in the $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CCH_2]^+$ system no such stabilization is available in terms of a suitable out-of-phase combination of Mo and Co d_{z^2} orbitals. Thus any migration of the

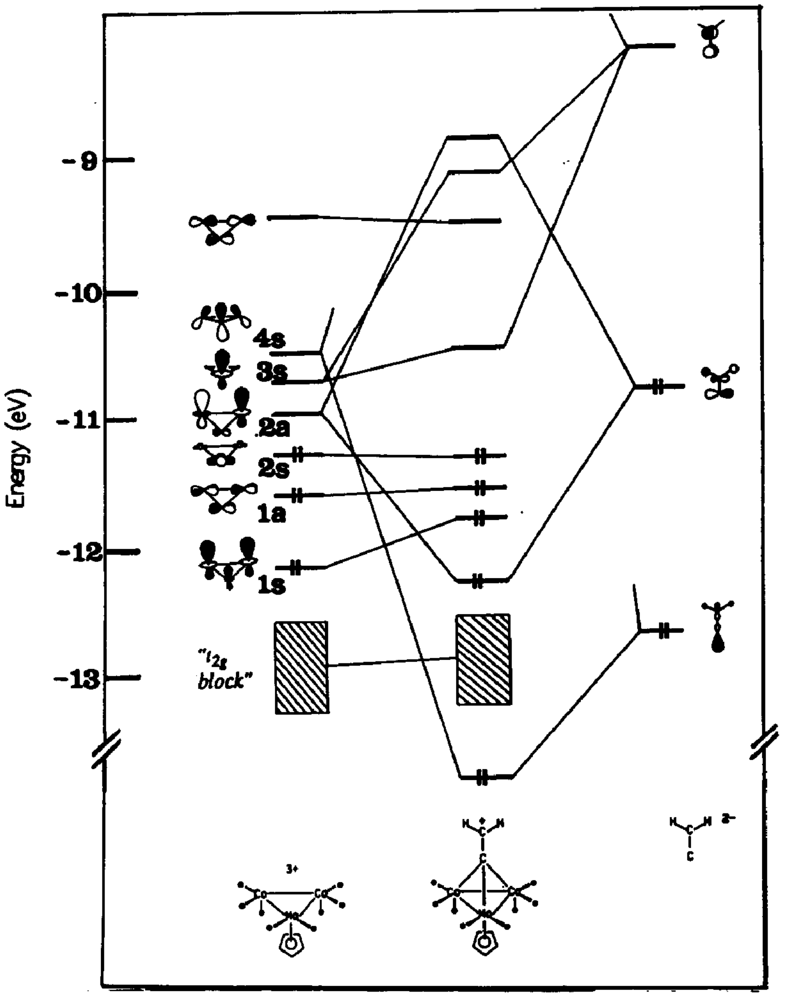

Fig. 4. Orbital interaction diagram showing the formation of $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CCH_2]^+$ from $[(C_5H_5)Mo(CO)_2Co_2(CO)_6]^{3+}$ and $[CH_2{=}C]^{2-}$ fragments.

$C{=}CH_2$ group between these two metals must inevitably surmount a rather large barrier.

To conclude, therefore, the vinylidene capping unit is particularly well stabilized by direct interaction with the molybdenum atom while migration to a cobalt centre is severely disfavored. These EHMO results are in excellent accord with the experimental data and together they provide us with a consistent picture of these fascinating cationic clusters.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use [25]. ^{13}C NMR spectra were recorded using Bruker AM500, WM250 and AC200 spectrometers. ^1H NMR spectra were recorded using Bruker AM500 and AC200 spectrometers. Chemical shifts reported were

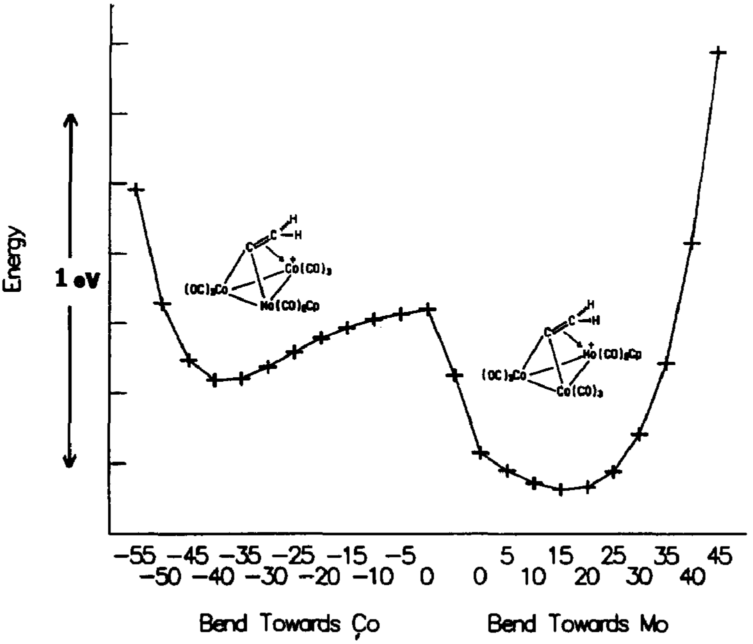

Fig. 5. Energy level diagram showing the effect of the tilt angle (in degrees) of the capping vinylidene unit from the axis perpendicular to the plane of the metals in the cationic clusters **19a** and **19b**.

referenced to tetramethylsilane. Infrared spectra were recorded on a Perkin Elmer 283 instrument using KBr solution cells. Mass spectra were obtained with a double focussing VG ZAB-E mass spectrometer under positive ion fast atom bombardment (FAB +) and negative ion fast atom bombardment (FAB-) conditions. 3-Nitrobenzyl alcohol was used as the matrix and xenon was the bombarding species. Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

(2-*endo*-Propynylborneol)[$Co_2(CO)_6$] (**4**), (H-C≡C-CH_2OH)[(C_5H_5)Mo$(CO)_2$Co$(CO)_3$] (**13**), (HC≡CCH_2OH) [($C_5H_4CH_3$)W$(CO)_2$Co$(CO)_3$] (**14**), (HC≡CCH(OH)(CH_2CH_3))[(C_5H_5)W$(CO)_2$Co$(CO)_3$] (**17**) and [$Co_3(CO)_9$CC-(CH_3)=CH_2] (**20**) were prepared as previously reported [8,16].

Protonation of (2-endo-propynylborneol)[$Co_2(CO)_6$] (4) to give 3.

A sample of (2-*endo*-CH_3C≡C-borneol)[$Co_2(CO)_6$] (**4**) (0.20 g, 0.4 mmol) was dissolved in CD_2Cl_2 (1.0 cm^3), filtered into a 5 mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of N_2 in a glovebag, 4–5 drops of HBF_4-Et_2O were added to the sample. The tube was then transferred to the spectrometer (AM 500) where the probe temperature had already been cooled to −40 ° C. After allowing the temperature of the NMR sample to stabilize at −40 ° C, the spectra of the cation **5** were recorded. ^{13}C NMR (CD_2Cl_2, −40 ° C): δ 194.4, 192.2 (carbonyls); 180.3 (C-2); 103.9, 102.9 (alkyne quaternary C's); 64.5 (C-1); 52.1 (C-7); 44.5 (C-3); 43.7 (C-4); 39.8 (C-6); 27.5 (C-5); 21.4 (alkyne CH_3); 20.3, 19.3 (C-8 and C-9); 13.2 (C-10). ^1H NMR (CD_2Cl_2, −40 ° C) [26*]: δ 2.86 (s, 3H, alkyne CH_3); 2.57 (m, 1H, H-3*x*); 2.19 (m, 1H, H-4); 2.12 (m, 1H, H-5*x*); 2.10 (m, 1H; H-6*x*); 2.01 (m, 1H, H-3*n*); 1.57 (m, 1H, H-5*n*); 1.36 (m, 1H, H-6*n*); 1.03 (s,

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* Reference numbers with an asterics indicate a note in the list of references.

3H), 0.94 (s, 3H) (H-8 and H-9); 0.85 (s, 3H, H-10). The sample was removed from the spectrometer, immediately quenched with H_2O and allowed to warm to room temperature overnight. After decanting off the water layer, the solution was dried over $MgSO_4$ and then the solvent was removed. The ^{13}C NMR of the quenched sample was recorded and it was identified as the elimination product analogous to 7. ^{13}C NMR (CD_2Cl_2): δ 146.3 (C-2); 139.7 (C-3); 95.1, 86.9 (alkyne quaternary C's); 57.5, 57.2 (C-1 and C-7); 52.8 (C-4); 32.1 (C-5); 25.4 (C-6); 21.8, 19.6, 19.5 (alkyne CH_3, C-8 and C-9); 12.9 (C-10).

Preparation of (2-$CH_3C{\equiv}C$-norborn-2-ene)[$(C_5H_5)_2Mo_2(CO)_4$] (7)

A solution of $[(C_5H_5)Mo(CO)_3]_2$ (1.062 g, 2.17 mmol) in toluene (200 cm^3) was heated at reflux with a slow flow of N_2 passing over the surface for 24 h. At that time, 2-*endo*-propynylborneol (0.420 g, 2.18 mmol) dissolved in toluene/THF (15 cm^3/50 cm^3) was added and the mixture was stirred at reflux for a further 20 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 2/98) which showed the formation of the product as a red band (R_f 0.25). After cooling to room temperature, the solvent was removed and the residue extracted with pentane. Evaporation of the solvent and purification of the resultant solid by flash chromatography on silica gel (eluent, ether/pentane, 2/98) gave 7 as a red solid (0.453 g, 0.74 mmol, 34.1%). ^1H NMR (C_6D_6): δ 5.52 (d, 1H, H-3, $J_{3\text{-}4}$ = 3.3 Hz); 4.94 (s, 5H), 4.93 (s, 5H) (H's of cyclopentadienyl rings); 2.77 9d of d, 1H, H-4, $J_{4\text{-}3}$ = 3.3, $J_{4\text{-}5x}$ = 3.5 Hz; 2.66 (s, 3H, alkyne CH_3); 1.86 (d of d of d of d, 1H, H-5*x*, $J_{5x\text{-}4}$ = 3.5, $J_{5x\text{-}5n}$ = 11.5, $J_{5x\text{-}6x}$ = 8.6, $J_{5x\text{-}6n}$ = 3.6 Hz); 1.45 (d of d of d, 1H, H-6*x*, $J_{6x\text{-}5x}$ = 8.6, $J_{6x\text{-}5n}$ = 3.5 $J_{6x\text{-}6n}$ = 11.7 Hz); 1.24 (d of d of d, 1H, H-6*n*, $J_{6n\text{-}5x}$ = 3.6, $J_{6n\text{-}5n}$ = 9.2, $J_{6n\text{-}6x}$ = 11.7 Hz); 1.10 (d, of d of d, 1H, H-5*n*, $J_{5n\text{-}5x}$ = 11.5, $J_{5n\text{-}6x}$ = 3.5, $J_{5n\text{-}6n}$ = 9.2 Hz); 1.01 (s, 3H), 0.73 (s, 3H) (H-8 and H-9); 0.70 (s, 3H, H-10). ^{13}C NMR (C_6D_6): δ 234.3, 233.9, 230.8, 230.0 (carbonyls); 151.9 (C-2); 137.8 (C-3); 108.2 (alkyne quaternary C); 92.8, 92.3 (CH's of cyclopentadienyl rings); 60.8, 58.2, 57.2 (alkyne quaternary C, C-1 and C-7); 52.0 (C-4); 32.1 (C-5); 26.2 (C-6); 26.0 (alkyne CH_3); 20.4, 20.2 (C-8 and C-9); 14.0 (C-10). IR (CH_2Cl_2): ν(CO) at 1990(m), 1920(s) and 1830(m) cm^{-1}. Mass spectrum (FAB +): (*m*/*z*)(%) 608(12) $C_{27}H_{28}O_4Mo_2$ $(M)^+$; 552(74) $(M-2CO)^+$; 524(9) $(M-3CO)^+$; 496(100) $(M-4CO)^+$; 450(15) $(M+H-\text{norbornene}-CO)^+$; 421(10) $(M-\text{norbornene}-2CO)^+$. Analysis: Found: C, 53.20; H, 4.64; $C_{27}H_{28}O_4Mo_2$ calcd.: C, 53.30; H, 4.64%.

Protonation of (2-$CH_3C{\equiv}C$-norborn-2-ene)[$(C_5H_5)_2Mo_2(CO)_4$] (7) to give 8

A solution of (2-$CH_3C{\equiv}C$-norborn-2-ene)[$(C_5H_5)_2Mo_2(CO)_4$] (7, 0.30 g, 0.5 mmol) in CD_2Cl_2 (1.0 cm^3) was filtered into a 5 mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of N_2 in a glovebag, 4–5 drops of HBF_4-Et_2O was added to the solution. The tube was then transferred to the spectrometer (AM 500) where the probe temperature had already been cooled to 0 ° C. After allowing the temperature of the NMR sample to warm up and stabilize at 0 ° C the spectra of the cation 8 were recorded. ^1H NMR (CD_2Cl_2, 0 ° C): δ 5.60 (s, 5H), 5.56 (s, 5H) (H's of cyclopentadienyl rings); 2.89 (s, 3H, alkyne CH_3); 2.29 (m, 1H), 1.81 (m, 1H) (H-3*x* and H-3*n*); 2.03 (br, 1H), 1.23 (br, 1H) (H-6*x* and H-6*n*); 2.00 (br, 1H, H-4); 1.98 (br, 1H), 1.36 (br, 1H) (H-5*x* and H-5*n*); 0.92 (s, 3H), 0.80 (s, 3H) (H-8 and H-9); 0.82 (s, 3H, H-10). ^{13}C NMR (CD_2Cl_2, 0 ° C): δ 227.1, 226.5, 223.0, 220.0 (carbonyls); 181.7 (C-2); 94.0, 92.8 (CH's of cyclopentadienyl rings); 63.3, 51.4 (C-1 and C-7); 46.0 (C-3); 43.3 (C-4); 41.9 (C-6); 27.6 (C-5); 27.4 (alkyne CH_3);20.2, 19.3 (C-8 and C-9); 14.2 (C-10).

Protonation of $(HC\equiv CCH_2OH)[(C_5H_5)Mo(CO)_2Co(CO)_3]$ *(13) to give 15*

In a glove bag containing an atmosphere of N_2, a sample of $(HC\equiv CCH_2OH)$ $[(C_5H_5)Mo(CO)_2Co(CO)_3]$ (**13**, 0.15 g, 0.36 mmol) was dissolved in CD_2Cl_2 (1 cm^3) and filtered into a 5 mm NMR tube. HBF_4-Et_2O (4–6 drops) was added to the solution and the NMR spectra of the cation **15** were recorded. ^1H NMR (CD_2Cl_2, ambient temperature): δ 6.42 (s, 1H, alkyne CH); 5.84 (s, 5H, cyclopentadienyl ring H's); 5.77 (br, 1H) and 4.94 (br, 1H) (CH_2). ^{13}C NMR (CD_2Cl_2, ambient temperature): δ 216.2, 209.2 (molybdenum carbonyls); 198.9 (cobalt carbonyls); 132.0 (alkyne quaternary C); 92.1 (cyclopentadienyl ring CH's); 86.3 (CH_2); 83.1 (alkyne CH).

Protonation of $(HC\equiv CCH_2OH)[(C_5H_4CH_3)W(CO)_2Co(CO)_3]$ *(14) to give 16*

Under a N_2 atmosphere in a glovebag, a sample of $(HC\equiv CCH_2OH)$-$[(C_5H_4CH_3)W(CO)_2Co(CO)_3]$ (**14**, 0.16 g, 0.34 mmol) was dissolved in CD_2Cl_2 (1 cm^3) and filtered into a 5 mm NMR tube. HBF_4-Et_2O (4–6 drops) was added to the solution and the NMR spectra of the cation **16** were recorded. ^1H NMR (CD_2Cl_2, ambient temperature): δ 6.36 (s, 1H, alkyne CH); 6.27 (br, 1H), 5.18 (br, 1H) (CH_2); 5.92 (br, 1H), 5.78 (br, 1H), 5.73 (br, 1H), 5.68 (br, 1H) (ring H's); 2.42 (s, 3H, ring CH_3). ^{13}C NMR (CD_2Cl_2, $-20\,^\circ C$): δ 203.0, 194.9 (tungsten carbonyls); 197.3 (cobalt carbonyls); 132.7 (alkyne quaternary C); 107.8 (ring quaternary C); 90.5, 89.0, 88.7, 87.9 (ring CH's); 84.9 (CH_2); 72.7 (alkyne CH).

Protonation of $(HC\equiv CCH(OH)(CH_2CH_3))[(C_5H_5)W(CO)_2Co(CO)_3]$ *(17) to give 18*

A sample of $(HC\equiv CCH(OH)(CH_2CH_3))[(C_5H_5)W(CO)_2Co(CO)_3]$ (**17**, the major diastereomer isolated in the substitution reactions) was dissolved in CD_2Cl_2 (1 cm^3), filtered into a 5 mm NMR tube and cooled in a dry ice/acetone bath. Under an atmosphere of N_2 in a glovebag, 4 drops of HBF_4-Et_2O were added to the solution. The tube was then transferred to the spectrometer where the probe had been cooled to $-40\,^\circ C$. After allowing the temperature to stabilize, the ^{13}C NMR spectra of the cation **18** were recorded. (The spectra indicated the presence of major and minor cationic diastereomers and the chemical shifts for the latter are indicated by the square brackets.) ^{13}C NMR (CD_2Cl_2, $-40\,^\circ C$): δ 202.3, 194.9 [201.5, 195.9] (tungsten carbonyls); 197.7 [197.7] (cobalt carbonyls); 122.6 [123.2] (alkyne quaternary C); 118.7 [121.0] (-*C*HEt); 90.9 [88.9] (ring CH's); 73.9 [71.6] (alkyne CH); 28.9 [37.3] (CH_2); 15.4 [17.2] (CH_3).

Preparation of $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3)=CH_2]$ *(21)*

A sample of $[Co_3(CO)_9CC(CH_3)=CH_2]$ (**20**, 0.964 g, 2.0 mmol) dissolved in THF (10 cm^3) was added to a solution of $(C_5H_5)Mo(CO)_3Na$ in 50 cm^3 of THF (prepared as described previously [8] by using 2.0 mmol of $[(C_5H_5)Mo(CO)_3]_2$ and finely divided Na metal) and the mixture was stirred at reflux for 45 min under an atmosphere of N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 5/95) which indicated the formation of the product as a green band (R_f 0.32). After cooling the solution to room temperature and removing the solvent, the crude solid was purified by flash chromatography on silica gel (eluent, ether/

pentane, 3/97) to give the product **21** as a green solid (0.681 g, 1.22 mmol, 61.0%). ^{1}H NMR (C_6D_6): δ 5.04 (br, 1H), 4.72 (br, 1H) (CH_2); 4.48 (s, 5H, ring H's); 2.06 (s, 3H, CH_3). ^{13}C NMR (C_6D_6): δ 163.5 (alkene quaternary C); 111.3 (CH_2); 92.1 (ring CH's); 28.6 (CH_3). I.R. (CH_2Cl_2): ν(CO) at 2075(w), 2060(w), 2020(m), 2010(s), 2005(s), 1940(br, sh), 1885(br) cm^{-1}. Mass spectra: (FAB +): (m/z)(%) 558(4) $C_{17}H_{10}O_8Co_2Mo$ $(M)^+$; 530(20) $(M-CO)^+$; 502(57) $(M-2CO)^+$; 474(100) $(M-3CO)^+$; 446(75) $(M-4CO)^+$; 418(48) $(M-5CO)^+$; 390(28) $(M-6CO)^+$; 362(17) $(M-7CO)^+$; 334(24) $(M-8CO)^+$. (FAB −): (m/z)(%) 530(100) $C_{17}H_{10}O_8Co_2Mo$ $(M-CO)^+$; 502(83) $(M\text{-}2CO)^+$; 474(72) $(M-3CO)^+$; 446(63) $(M-4CO)^+$; 418(23) $(M-5CO)^+$.

Preparation of $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3)_2]^+$ PF_6^- *(19)*

Using a syringe, 60% HPF_6 (0.10 cm^3, 0.67 mmol) was added to a solution of $[(C_5H_5)Mo(CO)_2Co_2(CO)_6CC(CH_3){=}CH_2]$ (**21**, 0.298 g, 0.53 mmol) in propionic anhydride (4 cm^3) under an N_2 atmosphere. The solution was stirred for 0.5 h during which time a noticeable quantity of the desired precipitate was observed to form. In order to ensure maximum precipitation of the salt, dry ether (15 cm^3) was added. The mixture was filtered under nitrogen and the product was further washed with anhydrous ether (15 cm^3). After being dried in vacuo at room temperature for 1 h, the solid was collected and transferred to a 10 mm NMR tube. It was subsequently dissolved in a mixture of SO_2 (5 cm^3) and CD_2Cl_2 (1 cm^3) (the latter added to provide a lock signal) and the NMR tube was sealed. The sample was transferred to the spectrometer (WM250) where the probe had been cooled to 0 °C and, after allowing time for the temperature to stabilize, the ^{13}C NMR spectra of **19** were recorded. ^{13}C NMR (0 °C): δ 203.7 (broad, molybdenum and cobalt carbonyls); 153.0 (CMe_2); 96.0 (ring CH's); 35.3 (CH_3's). ^{13}C NMR (−90 °C): δ 296.0 (alkylidyne quaternary C); 198.7 (broad, molybdenum and cobalt carbonyls); 147.5 (CMe_2); 95.4 (ring CH's); 34.7 (CH_3's).

Preparation of $[Co_3(CO)_9CC(CH_3)_2]^+$ PF_6^- *[16]*

Under an atmosphere of N_2, 60% HPF_6 (0.14 cm^3, 0.95 mmol) was added to solution of $[Co_3(CO)_9CC(CH_3){=}CH_2]$ (0.350 g, 0.73 mmol) in propionic anhydride (4 cm^3). After stirring for 0.5 h, ether (15 cm^3) was added to ensure complete precipitation of the salt and then the mixture was filtered under nitrogen. After washing the solid with additional ether (20 cm^3), the sample was dried in vacuo for 1 h at room temperature and then transferred into a 10 mm NMR tube. The salt was dissolved in a mixture of SO_2/CD_2Cl_2 (5 cm^3/1 cm^3), the NMR tube was sealed and the spectra recorded. ^{13}C NMR (−110 °C): δ 197.8 (3 carbonyls), 191.5 (6 carbonyls); 149.6 (CMe_2); 33.2 (CH_3's).

X-ray crystallography

Crystals of (2-$CH_3C{\equiv}C$-norborn-2-ene)$[(C_5H_5)_2Mo_2(CO)_4]$ (7) were grown from hexane/CH_2Cl_2. The density was determined by suspension in an aqueous solution of $ZnCl_2$. Purple-black prismatic crystals were examined under a polarizing microscope for homogeneity. A well formed crystal, 0.23 × 0.32 × 0.35 mm, was selected and sealed in a Lindemann capillary. Unit cell parameters were obtained from a least squares fit of χ, ϕ, and 2θ for 15 reflections in the range $(20.8 < 2\theta < 27.4°)$ recorded on a Nicolet P3 diffractometer with use of graphite monochromated

Mo-K_α radiation ($\lambda = 0.71069$ Å at 22° C). Intensity data were also recorded on a Nicolet $P2_1$ diffractometer with a coupled θ(crystal)–2θ(counter) scan, for 5056 reflections in the quadrant (h, $k \pm l$) with $2\theta \leq 50°$. The method of selection of scan rates and initial data treatment have been described [27,28]. Corrections for Lorentz-polarization effects and absorption (ψ-scans) [29] were applied to all reflections. Two standard reflections (0, −8, 0; 2.55% and −3, −6, 1; 2.36%) monitored every 48 reflections showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (28) were excluded and 678 symmetry-equivalent data were then averaged ($R_{\text{int}} = 0.0098$) to give 4350 unique reflections. A summary of crystal data is given in Table 1.

The coordinates of the molybdenum atoms were found from a three-dimensional Patterson synthesis with use of the program SHELXS-86 [30]. Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron density synthesis revealed all the non-hydrogen atoms. After refinement the temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic and further cycles of refinement revealed the positional parameters for all of the hydrogen atoms. These were included in subsequent cycles of refinement (U fixed at 0.08 Å^2). Further refinement using full-matrix least-squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error reached 0.004. Correction for secondary extinction was made by the method in SHELX-76 [31]. Final $R_1 = 0.0290$, $R_2 = 0.0276$ for 4350 reflections. Alternative refinement where coordinates x, y, z were replaced by $-x, -y, -z$ gave $R_1 = 0.0301$, $R_2 = 0.0286$, and $S = 1.1661$ (for definition see Table 3) for 4350 reflections, confirming the assignment for the correct hand of the structure. Throughout the refinement, scattering curves were taken from Ref. 32 and anomalous dispersion corrections from Ref. 33 were applied to the curve for molybdenum. All calculations were performed on a VAX 8650 computer. Programs used: XTAL [34], data reduction; TAPER [29], absorption correction; SHELX-86 [30], structure solution; SHELX-76 [31], structure refinement: MOLGEOM [35], molecular geometry and SNOOPI [36], diagrams. Final atomic positional parameters are given in Table 2, selected bond lengths and bond angles are given in Table 3.

Molecular orbital calculations

All calculations were carried out within the Extended Hückel formalism [37,38] using the weighted H_{ij} formula [39]. The bond lengths and angles were taken from the X-ray crystal structure of $(C_5H_5)Mo(CO)_2Co_2(CO)_6CPh$ [40]. The atomic parameters used were taken from Ref. 41.

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Supplementary material available

Tables S1–S5 listing full crystal data, least-squares mean planes and dihedral/torsional angles, hydrogen atom positional parameters, bond lengths and bond angles involving hydrogen atoms and anisotropic temperature factors respectively (10 pages); Table S6, observed and calculated structure factor amplitudes (27 pages). These data are available from the authors.

References and notes

1 D. Seyferth, Adv. Organomet. Chem., 14 (1976) 97.
2 B.E.R. Schilling and R. Hoffmann, J. Am. Chem. Soc., 101 (1979) 3456.
3 R.T. Edidin, J.R. Norton and K. Mislow, Organometallics, 1 (1982) 561.
4 M.F. D'Agostino, M. Mlekuz, J.W. Kolis, B.G. Sayer, C.A. Rodger, J.-F. Halet, J.-Y. Saillard and M.J. McGlinchey, Organometallics, 5 (1986) 2345.
5 K.M. Nicholas, Acc. Chem. Res., 20 (1987) 207.
6 S.L. Schreiber, M.T. Klimas and T. Sammakia, J. Am. Chem. Soc., 109 (1987) 5749.
7 A. Meyer, D.J. McCabe and M.D. Curtis, Organometallics, 6 (1987) 1491.
8 M.F. D'Agostino, C.S. Frampton and M.J. McGlinchey, Organometallics, in press.
9 J.F. King and P. de Mayo, in P. de Mayo (Ed.), Molecular Rearrangements, Interscience, New York, 1967, Ch. 13.
10 M. Savignac, G. Jaouen, C.A. Rodger, R.E. Perrier, B.G. Sayer and M.J. McGlinchey, J. Org. Chem., 51 (1986) 2328.
11 G. Jaouen and M. Gruselle, private communication.
12 W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton and L.A. Rankel, J. Am. Chem. Soc., 100 (1978) 5764.
13 W.I. Bailey, Jr., F.A. Cotton, J.D. Jamerson and J.R. Kolb, J. Organomet. Chem., 121 (1976) C23.
14 W.I. Bailey Jr., D.M. Collins and F.A. Cotton, J. Organomet. Chem., 135 (1977) C53.
15 M.F. D'Agostino, K.L. Malisza and M.J. McGlinchey, in preparation.
16 D. Seyferth, C.S. Eschbach, G.H. Williams and P.L.K. Hung, J. Organomet. Chem., 134 (1977) 67.
17 S. Padmanabhan and K.M. Nicholas, J. Organomet. Chem., 268 (1983) C23.
18 (a) V.I. Sokolov, I.V. Barinov and O.A. Reutov, Isv. Akad. Nauk SSR, Ser Khim, (1982) 1922; (b) O.A. Reutov, I.V. Barinov, V.A. Chertkov and V.I. Sokolov, J. Organomet. Chem., 297 (1985) C25.
19 S.F.T. Froom, M. Green, K.R. Nagle and D.J. Williams, J. Chem. Soc., Chem. Commun., (1987) 1305.
20 R.M. Moriarty, Y.-Y. Ku, U.S. Gill, R. Gilardi, R.E. Perrier and M.J. McGlinchey, Organometallics, 8 (1989) 960.
21 E. Delgado, J.C. Jeffery and F.G.A. Stone, J. Chem. Soc., Dalton Trans., 10 (1986) 2105.
22 W. Bernhardt and H. Vahrenkamp, Angew. Chem., Int. Ed. Engl., 23 (1984) 141.
23 M. Mlekuz, P. Bougeard, B.G. Sayer, S. Peng, M.J. McGlinchey, A. Marinetti, J.-Y. Saillard, J. Ben Naceur, B. Mentzen and G. Jaouen, Organometallics, 4 (1985) 1123.
24 J.-F. Halet, J.-Y. Saillard, R. Lissillour, M.J. McGlinchey and G. Jaouen, Inorg. Chem., 24 (1985) 218.
25 D.D. Perrin, W.L.F. Armarego and D.D. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York, 1980.
26 *exo* Hydrogens (H*x*) are situated proximal to the dimethyl bridge; analogously, *endo* hydrogens (H*n*) occupy positions away from the bridging group.
27 B. Lippert, C.J.L. Lock, B. Rosenburg and M. Zvagulis, Inorg. Chem., 16 (1977) 1525.
28 R.P. Hughes, N. Krishnamachari, C.J.L. Lock, J. Powell and C.T. Turner, Inorg. Chem., 16 (1977) 314.
29 J.C. Calabrese and R.M. Burnett, TAPER locally modified by Z. Tun with the permission of Nicolet XRD Corp., 1980.
30 G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, University of Göttingen, Federal Republic of Germany, 1986.
31 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, England, 1976.
32 D.T. Cromer and J.B. Mann, Acta Cryst. A, 24 (1968) 231.

33 D.T. Cromer and D. Liberman, J. Chem. Phys., 53 (1970) 1891.

34 J.M. Stewart and S.R. Hall, The XTAL System of Crystallographic Programs. Tech. Rept. TR-1364, University of Maryland, College Park, U.S.A., 1983.

35 J. Stephens, MOLGEOM adapted from CUDLS, McMaster University, Canada, 1973.

36 K. Davies, CHEMGRAF suite: SNOOPI, Chemical Design Ltd. Oxford, England, 1983.

37 R. Hoffmann, J. Chem. Phys., 39 (1963) 1397.

38 R. Hoffmann and W.N. Lipscomb, J. Chem. Phys., 36 (1962) 2179 and 3489.

39 J.H. Ammeter, H.-B. Bürgi, J.C. Thibeault and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 3686.

40 H. Beurich and H. Vahrenkamp, Angew. Chem., Int. Ed. Engl., 17 (1978) 863.

41 J.-F. Halet, J.-Y. Saillard, R. Lissillour, M.J. McGlinchey and G. Jaouen, Inorg. Chem., 24 (1985) 218.