frared spectrum of **10** shows two bands in the ν(CO) region in about the same positions as those for compound **5**. On this basis, it was initially thought that **10** should be formulated as $[W(CO)_3(OPh)]_n^{n-}$. However, its elemental analyses (see footnote *d* of Table III) and ^1H NMR spectrum (Table II)[21] provide strong support for the dinuclear formulation.

The infrared spectrum of **10** is similar to that reported for the previously mentioned $K_3[W_2(CO)_6(\mu\text{-}OH)_3]\cdot 2H_2O$ (ν(CO) 1840, 1700 cm^{-1}). The structure of $W_2(CO)_6(\mu\text{-}OH)_3{}^{3-}$ consists of three doubly bridging hydroxy groups bound to two essentially noninteracting tungsten atoms, each containing three terminal CO groups. It seems likely that compound **10** adopts the same basic structure as the hydroxy derivative. It was noted briefly in the Experimental Section that attempts to isolate species such as $[M(CO)_3OH]_n^{n-}$ or $[M_2(CO)_6(OH)_3]^{3-}$ (M = Cr, Mo, W) from the complex product mixtures obtained in the reactions of OH^- with corresponding $M(CO)_3PMTA$ or $M(CO)_3(CH_3CN)_3$ have been unsuccessful.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant CHE79-12159) for support of this research. We also thank the NSF for partial support of the Enraf-Nonius X-ray diffraction and structure solving equipment (NSF Grant CHE77-28505). We are indebted to Professors Doyle Britton and Lou Pignolet and Mr. Mike McGuiggan for many discussions and assistance concerning the X-ray crystal structure study.

Registry No. 1, 81097-65-6; 2, 81097-67-8; 3, 81097-69-0; 4, 81097-71-4; 5, 81097-73-6; 6, 81097-75-8; 7, 81097-77-0; 8, 81097-79-2; 9, 81097-81-6; 10, 81097-83-8; $Cr(CO)_3PMTA$, 15225-94-2; $Mo(CO)_3PMTA$, 81120-72-1; $W(CO)_3PMTA$, 81097-61-2; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

Supplementary Material Available: Tables of weighted least-squares planes and the distances of the atoms from their respective planes, root-mean-square amplitudes of thermal vibration, and observed and calculated structure factors for the structure of $[Me_4N]_3[W(CO)_3(OEt)]_3$ (19 pages). Ordering information is given on any current masthead page.

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[21] The ratio of the integrated phenyl group hydrogens to the tetraethylammonium cation hydrogens is very close to that expected for a 1:1 ratio of C_6H_5 to Et_4N^+.

Structure and Properties of Tricarbonyl(2–5:9,10-η-9-methylenebicyclo[4.2.1]nona-2,4,7-triene)chromium(0). New Chromium–Olefin Stereochemistry

Geoffrey B. Jameson* and Albrecht Salzer

Department of Inorganic Chemistry, University of Zurich, CH 8057 Zurich, Switzerland

Received October 29, 1981

Tricarbonyl(2–5:9,10-η-9-methylenebicyclo[4.2.1]nona-2,4,7-triene)chromium(0), prepared by the reaction of $Cr(CO)_3(CH_3CN)_3$ with the tetraolefinic ligand I, crystallizes in space group *C*2/*c* in a unit cell with dimensions a = 25.682 (5) Å, b = 6.850 (2) Å, c = 14.263 (3) Å, β = 115.90 (1)°, and Z = 8. Structural parameters for the molecule, including hydrogen atoms, were refined on F (2370 data in the range $0.043 < \lambda^{-1} \sin\theta < 0.7261$ Å^{-1} having $F_o^2 > 3\sigma(F_o^2)$) to final values for R and R_w of 0.040 and 0.048. Coordination is approximately octahedral with three mutually cis carbonyl ligands and with the butadiene and the semicyclic moieties coordinated: $Cr–C_{CO}(av)$ = 1.847 (14, 3) Å; $Cr–C_{but}(av)$ 2.367 (11, 3) (outer) and 2.200 (1, 3) Å; $Cr–C_{methylene}$ = 2.339 (2) and 2.386 (3) Å. When given, the first number in parentheses is the estimated standard deviation derived from the scatter of parameters about their mean and the second is the estimated standard deviation of an individual parameter. The C═C vector for the semicyclic olefin is approximately perpendicular to those for the butadiene group—this stereochemistry is unusual, since endo coordination to the bishomobenzene system is also feasible. Stereochemical arguments are presented in favor of the preferential exo approach toward the butadiene group. The unusual ^{13}C NMR high-field coordination shift of the quaternary carbon resonance of the semicyclic olefin (106 ppm compared to that for the free olefin) is attributed to shielding effects.

Introduction

It is often true that the products of chemical reactions fail to conform to the experimenters' predictions—witness the exponentially increasing numbers of crystal structures of compounds which have proved relatively intractable to conventional spectroscopic analysis. This is particularly true for organometallic reactions, where the variable coordination numbers, stereochemistries, and oxidation states of a metal center conspire to give greater scope for predictive disasters and hence to hinder attempts to systematize and understand mechanisms of organometallic reactions.

For example, given a multiolefin molecule, where the number of double bonds which could coordinate exceeds the number of coordination sites available, what stereochemistry may be expected? For the case of coordination of olefins to platinum species, which has long been of interest, considerable insight into the stereochemistry and reactivity of such complexes now exists.[1,2] The same cannot be said for olefin coordination to many other transition-metal species. Here we wish to consider the coordination of the tetraolefin 9-methylenebicyclo[4.2.1]nona-2,4,7-triene I to the well-known trienophilic $M(CO)_3$ (M = Cr, Mo) species.

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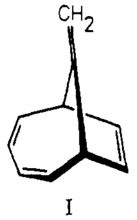

I

Two very different modes of coordination are sterically feasible for the formation of a monomeric $M(CO)_3$(triolefin) complex. In the parallel mode the C=C vector of the cyclic olefin lies approximately parallel to the butadiene plane to give a pseudobishomobenzene species; in the perpendicular mode the C=C vector of the semicyclic olefin lies approximately perpendicular to the butadiene group.

Almost all olefin complexes of the $M(CO)_3$ species have involved conjugated trienes[3-10] or pseudotriene systems.[11-15,18-24] The single exception appears to be the butadiene–olefin complex (5,6-dimethylenebicyclo[2.2.1]hept-2-ene)$Mo(CO)_3$.[17] In no instance has coordination of an olefin perpendicular to other coordinated olefins been structurally characterized for the $M(CO)_3$ systems; furthermore, we know of only several structures where this geometry is found—an RuCl(triolefin)[25] and a $PtCl_2$(diolefin)[26] species.

Thus, endo coordination of the tetraolefin I was expected, since this would yield the pseudobishomobenzene species. Our previous investigations into the stereochemistry and isomerizations of the $M(CO)_3$ compounds (M = Cr, Mo, W) had shown that a pronounced preference for this coordination mode existed, as thermal rearrangements of bicyclo[6.1.0]nona-2,4,6-triene complexes yielded compounds of bicyclo[4.2.1]nona-2,4,7-triene exclusively in very good yields.[27,28] This type of rearrangement is not observed in the free hydrocarbon or in the iron tricarbonyl or cyclopentadienylcobalt complex of this ligand.[29,30] Olefin I can be regarded as a bicyclic derivative of cycloocta-1,3,6-triene, whose $M(CO)_3$ complexes (M = Cr, Mo, Fe) we have also reported previously.[28,29]

Table I. Crystal Data and Data Collection Parameters

formula	$CrC_{13}O_3H_{10}$
fw	266.2 amu
space group	C_{2h}^6-$C2/c$
a	25.682 (5) Å
b	6.850 (2) Å
c	14.263 (3) Å
β	115.90 (1)°
V	2257 Å^3
Z	8
temp	19 °C
cryst shape	flattened hexagonal needle, 0.13 × 0.20 × 0.54 mm
cryst vol	0.0124 mm^3
radiation	graphite-monochromated Mo Kα (λ = 0.7093 Å)
linear abs coeff	9.79 cm^{-1}
transmission factors	0.823–0.895
scan speed	2.0°/min in 2θ
λ^{-1} sin θ limits	0.0431–0.7261 Å^{-1} (3.5° < 2θ < 62.0°)
bkgd counts	10 s each side of peak with rescan option[a]
scan range	1.1° below Kα_1 to 0.9° above Kα_2
data collected	$\pm h, -k, +l$
p	0.04
unique data	3917
unique data with $F_o^2 > 3\sigma(F_o^2)$	2370

[a] Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568.

^{13}C NMR measurements of $Cr(CO)_3(C_{10}H_{10})$ and the molybdenum analogue surprisingly indicated that the metal tricarbonyl unit had exclusively adopted an exo coordination mode; that is, the semicyclic double bond and the butadiene group were coordinated.[31] Here we confirm the NMR assignment, and, through the structure analysis, some light is shed on the geometry and properties of this unusual ligand as well as the ligand properties of the $M(CO)_3$ (M = Cr, Mo) moieties. As no previous X-ray structure analysis of a bicyclo[4.2.1]nona-2,4,7-triene derivative existed so far, we also obtained additional insight into the stereochemistry of this rather strained polyolefin system.

Experimental Section

Preparation of $Cr(CO)_3(C_{10}H_{10})$. Ligand I was prepared following the procedure given by Schechter.[32] On treatment with an excess of $Cr(CO)_3(CH_3CN)_3$ in THF, a rapid color change was observed. After workup and extraction with *n*-hexane, red crystals of $Cr(CO)_3(C_{10}H_{10})$ precipitated at −30 °C. Single crystals were grown from hexane by cooling a saturated and filtered solution slowly from 20 to 5 °C. The ^{13}C NMR spectrum was reported previously by A.S.;[31] the assignment of signals was based on

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Table II. Final Positional Parameters for $Cr(CO)_3(C_{10}H_{10})$

ATOM	X[A]	Y	Z
CR	0.104485(15)	0.238051(53)	0.662845(27)
C1	0.12964(11)	0.44013(38)	0.60711(19)
C2	0.03435(12)	0.35376(43)	0.63993(21)
C3	0.06492(11)	0.16156(40)	0.52653(19)
O1	0.144524(95)	0.55954(33)	0.56727(17)
O2	-0.00991(10)	0.41970(41)	0.62144(20)
O3	0.038773(88)	0.12248(35)	0.43948(15)
C10	0.08801(11)	0.00650(38)	0.76941(20)
C11	0.10591(11)	-0.07389(37)	0.70021(20)
C12	0.15670(11)	-0.02831(37)	0.68638(20)
C13	0.19956(11)	0.10622(41)	0.74130(20)
C14	0.21386(11)	0.17509(43)	0.85050(20)
C15	0.15829(11)	0.26159(38)	0.84360(17)
C16	0.13859(14)	0.44448(42)	0.81254(21)
C17	0.22333(12)	0.00715(47)	0.92519(21)
C18	0.17668(13)	-0.03107(44)	0.93719(20)
C19	0.12737(11)	0.10277(40)	0.87166(19)
H11	0.0815(12)	-0.1477(44)	0.6531(20)
H12	0.1571(11)	-0.0818(40)	0.6241(22)
H14	0.2426(13)	0.2730(40)	0.8720(23)
H16A	0.1029(14)	0.4850(47)	0.8162(23)
H16B	0.1634(13)	0.5342(45)	0.8012(23)
H17	0.2585(14)	-0.0499(46)	0.9603(24)
H18	0.1713(12)	-0.1292(43)	0.9760(21)
H19	0.1067(11)	0.1488(39)	0.9026(20)
H10	0.0526(11)	-0.0222(35)	0.7580(18)
H13	0.2280(12)	0.1357(45)	0.7161(22)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES.

off-resonance experiments as well as other decoupling techniques.

Crystallographic Study of $Cr(CO)_3(C_{10}H_{10})$. Symmetry and systematic absences consistent with the space groups C_s^4—*Cc* and C_{2h}^6—*C2/c* were observed with precession and Weissenberg photography. Lattice parameters and the precise orientation of the crystal upon the Picker FACS-I diffractometer were derived from the setting angles of 17 automatically centered reflections in the range $0.4369 < \lambda^{-1} \sin\theta < 0.4583$ Å^{-1}. Other important features of data collection are summarized in Table I. Standard programs (a local version of the Northwestern University system[33]) and procedures were used to solve and refine the structure, with all calculations being performed on the University of Zurich's IBM 3033 computer. Interestingly, MULTAN 78 solutions were uninterpretable when all data were utilized. However, when data $2\theta \leq 40°$ ($\lambda^{-1} \sin\theta \leq 0.4822$ Å^{-1}) were used, the whole molecule was apparent; the less precisely measured high angle data had yielded some spuriously high *E* values. We also note a recent counter example to this where it was not until data with $2\theta \geq 40°$ (λ^{-1} sin $\theta \geq 0.4822$ Å^{-1}) were included that a recognizable solution appeared, despite, in this case, the input of considerable (correct) molecular information for the calculation of *E* values.[34]

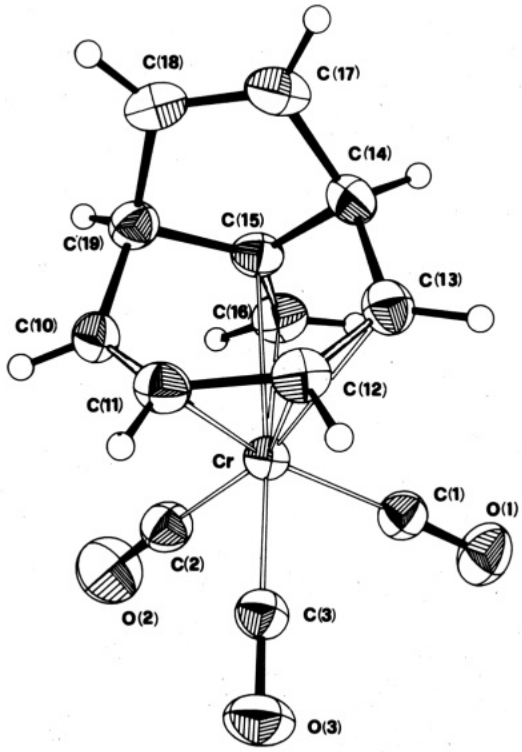

Figure 1. Molecular diagram and atom labeling scheme for $Cr(CO)_3(C_{10}H_{10})$. Thermal ellipsoids are drawn at the 50% probability level, except for hydrogen atoms which are artificially small.

Table V. Bond Distances (Å) for $Cr(CO)_3(C_{10}H_{10})$

Cr–C(1)	1.848 (3)	C(10)–C(19)	1.515 (4)
Cr–C(2)	1.861 (3)	C(14)–C(15)	1.508 (4)
Cr–C(3)	1.833 (3)	C(15)–C(19)	1.501 (4)
Cr–C(10)	2.359 (3)	C(14)–C(17)	1.514 (4)
Cr–C(11)	2.199 (3)	C(19)–C(18)	1.511 (4)
Cr–C(12)	2.201 (3)	C(17)–C(18)	1.309 (4)
Cr–C(13)	2.375 (3)	C(10)–H(10)	0.87 (2)
Cr–C(15)	2.339 (2)	C(11)–H(11)	0.86 (3)
Cr–C(16)	2.386 (3)	C(12)–H(12)	0.97 (3)
C(1)–O(1)	1.152 (3)	C(13)–H(13)	0.97 (3)
C(2)–O(2)	1.142 (3)	C(14)–H(14)	0.94 (3)
C(3)–O(3)	1.156 (3)	C(16)–H(16A)	0.98 (3)
C(10)–C(11)	1.373 (3)	C(16)–H(16B)	0.95 (3)
C(12)–C(13)	1.386 (4)	C(17)–H(17)	0.91 (3)
C(15)–C(16)	1.351 (4)	C(18)–H(18)	0.92 (3)
C(11)–C(12)	1.436 (4)	C(19)–H(19)	0.88 (3)
C(13)–C(14)	1.511 (4)		

All hydrogen atoms were easily located in a penultimate difference Fourier map. Least-squares refinements converged at values for *R* and R_w on *F* of 0.040 and 0.048 for a model comprising 17 nonhydrogen atoms with anisotropic thermal parameters, 10 hydrogen atoms with isotropic thermal parameters, and a parameter for secondary extinction—a total of 195 variable parameters. The final value for the error in an observation of unit weight was 1.36 e.

The final difference Fourier map had no significant features, and analysis of the agreement between F_o and F_c as functions of the magnitude of F_o and of $\lambda^{-1} \sin\theta$ showed no trends, indicating that the weighting scheme assumed was satisfactory. Final positional parameters are given in Table II. Table III lists the thermal parameters, and Table IV lists $10F_o$ vs. $10F_c$.[35]

Results and Discussion

General Description of the Structure. Three mutually cis carbonyl ligands, the butadiene, and semicyclic

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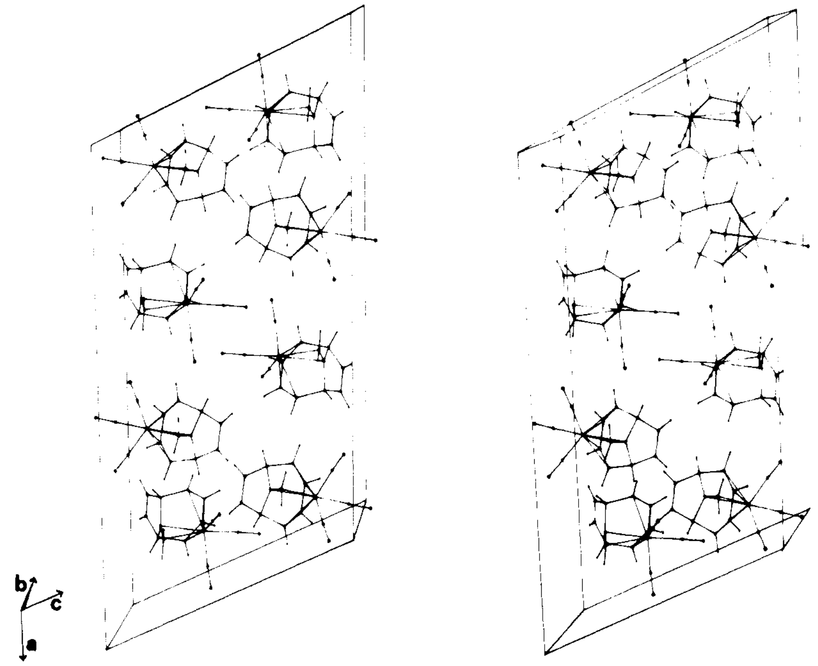

Figure 2. The arrangement of molecules of $Cr(CO)_3(C_{10}H_{10})$ with respect to the unit cell.

Table VI. Bond Angles (Deg) for $Cr(CO)_3(C_{10}H_{10})$

C(1)-Cr-C(2)	95.7 (1)	C(19)-C(10)-C(11)	125.1 (2)	H(13)-C(13)-C(14)	116 (2)
C(1)-Cr-C(3)	83.9 (1)	C(14)-C(13)-C(12)	124.4 (2)	H(11)-C(11)-C(12)	115 (2)
C(2)-Cr-C(3)	83.7 (1)	C(10)-C(11)-C(12)	128.4 (2)	H(12)-C(12)-C(11)	115 (2)
C(1)-Cr-*A*[a]	164.6	C(13)-C(12)-C(11)	127.7 (2)	H(11)-C(11)-C(10)	116 (2)
C(1)-Cr-*B*	101.3	C(18)-C(19)-C(10)	111.0 (2)	H(12)-C(12)-C(13)	117 (2)
C(1)-Cr-*C*	94.5	C(17)-C(14)-C(13)	112.3 (2)	H(14)-C(14)-C(13)	111 (2)
C(2)-Cr-*A*	99.7	C(13)-C(14)-C(15)	105.0 (2)	H(19)-C(19)-C(10)	110 (2)
C(2)-Cr-*B*	162.9	C(10)-C(19)-C(15)	105.5 (2)	H(14)-C(14)-C(15)	109 (2)
C(2)-Cr-*C*	92.2	C(17)-C(14)-C(15)	101.6 (2)	H(19)-C(19)-C(15)	112 (2)
C(3)-Cr-*A*	97.7	C(18)-C(19)-C(15)	101.9 (2)	H(14)-C(14)-C(17)	117 (2)
C(3)-Cr-*B*	100.0	C(14)-C(15)-C(16)	126.4 (3)	H(19)-C(19)-C(18)	116 (2)
C(3)-Cr-*C*	175.4	C(19)-C(15)-C(16)	126.4 (3)	H(16A)-C(16)-C(15)	118 (2)
A-Cr-*B*	63.9	C(14)-C(15)-C(19)	107.1 (2)	H(16B)-C(16)-C(15)	118 (2)
A-Cr-*C*	85.0	C(14)-C(17)-C(18)	111.7 (3)	H(16A)-C(16)-H(16B)	123 (3)
B-Cr-*C*	84.6	C(19)-C(18)-C(17)	111.4 (3)	H(17)-C(17)-C(14)	122 (2)
Cr-C(1)-O(1)	176.0 (2)	H(10)-C(10)-C(11)	115 (2)	H(18)-C(18)-C(19)	121 (2)
Cr-C(2)-O(2)	176.7 (3)	H(13)-C(13)-C(12)	118 (2)	H(17)-C(17)-C(18)	126 (2)
Cr-C(3)-O(3)	176.6 (2)	H(10)-C(10)-C(19)	119 (2)	H(18)-C(18)-C(17)	128 (2)

[a] *A*, *B*, and *C* are defined as the midpoints of the olefin bonds C(10)-C(11), C(12)-C(13), and C(15)-C(16), respectively.

methylene olefin moieties combine to give a pseudooctahedral coordination sphere around the chromium center, as illustrated in Figures 1 and 3 and tabulated in Tables V and VI (bond distances and angles). There exists a pseudo-mirror plane defined by atoms C(1), O(1), and Cr, which bisects the ligand I. The most striking feature, the exo mode of coordination adopted by the $Cr(CO)_3$ species, will be discussed below in more detail.

The packing of the molecules in the unit cell, illustrated in Figure 2, is quite tight, consistent with the excellent crystal mosaicity observed prior to data collection. Among the nonhydrogen atoms the following close contacts are noted: O(2)···O(3) = 3.252 (4) Å; O(1)···C(12) = 3.239 (4) Å; O(3)···C(19) = 3.227 (4) Å; including hydrogen atoms, O(1)···H(12) = 2.56 (3) Å. It is presumably through such contacts that the small deviations from mirror symmetry arise.

The Chromium-Olefin Moiety. Figure 3 clearly illustrates the conformation of the coordinated 9-methylenebicyclo[4.2.1]nona-2,4,7-triene molecule. Figure 4 shows bond distances and angles in the tetraolefin group. Departures from mirror symmetry are small and mostly of marginal significance.

Of more import is the conformation of this rather strained bicycle; the angle at the bridging carbon atom of the semicyclic double bond C(14)–C(15)–C(19) is only 107.1 (2)°; bond angles as small as 101.6 (2)° are observed at $C(sp^3)$ centers. While the butadiene moiety is almost planar (see Table VII for least-squares planes), atoms C(19) and C(14) are substantially out of this plane (see also Figure 3). As a result of this twist, the hydrogen atoms H(11), H(12), H(13), and H(14) are significantly displaced from the butadiene plane *toward* the chromium atom, whereas for the methylene group the hydrogen atoms show the more usual small displacement *away* from the metal. The five-membered ring defined by atoms C(14), C(15), C(17), C(18), and C(19) is also approximately planar (to within 0.2 Å); this was suggested earlier.[36] Table VIII quantifies the dihedral angles between various least-squares planes.

In the ^{13}C NMR spectrum of $Cr(CO)_3(C_{10}H_{10})$ a high-field shift of 106 ppm for the methylene carbon atom C(15) was observed upon coordination; for the terminal carbon

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(36) Hoffman, R. W.; Kurz, H. *Chem. Ber.* **1975**, *108*, 119–127.

Table VII. Least-Squares Planes

plane	coeff: $Ax + By + Cz - D = 0$[a]				atoms defining plane displacement[b]				other atoms displacement[b]					
	A	B	C	D										
but	6.125	-4.816	7.109	5.979	C(10) -002	C(11) 003	C(12) -004	C(13) 002	C(14) 534	C(19) 503	H(10) -161	H(11) -126	H(12) -186	H(13) -146
ene 1	1.233	2.018	11.946	10.784	C(14) -007	C(15) 017	C(16) -009	C(19) -007	H(16A) 072	H(16B) 066				
ene 2	-1.209	4.436	10.051	9.065	C(14) 002	C(17) -004	C(18) 004	C(19) -002	H(17) 053	H(18) -035	C(15) 383	C(16) 906		
plane 4	6.179	-6.148	3.243	2.992	C(13) -008	C(14) 011	C(10) 007	C(19) -010	C(12) 376	C(11) 388				

[a] The plane is in crystal coordinates as defined by: Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185-189. [b] The displacement in Å is generated by placing a decimal point in front of the first digit. The estimated standard deviations for the displacements of carbon atoms from their least-squares planes are 0.003 Å.

Table VIII. Dihedral Angles (Deg) between Planes

	but	ene 1	ene 2	plane 4
but	···	63.7	87.5	20.6
ene 1		···	23.9	84.3
ene 2			···	108.1

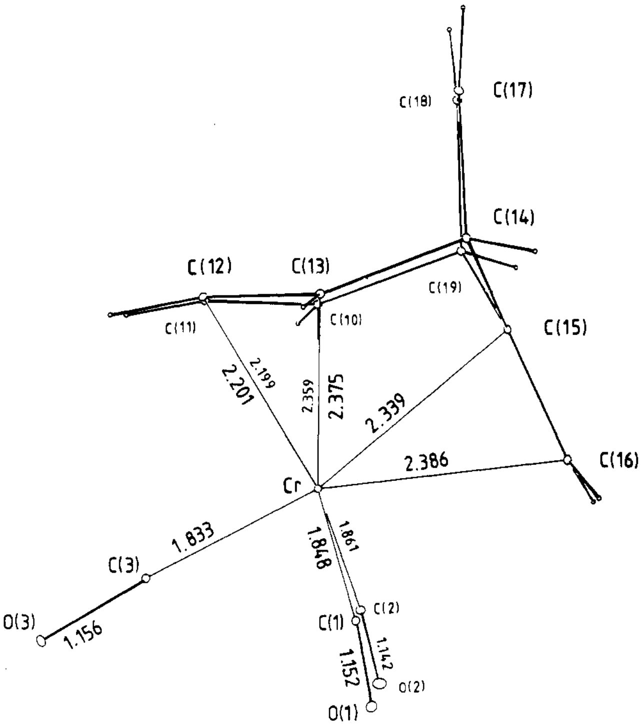

Figure 3. Conformation of the ligand I and Cr–C distances for the complex.

atom the shift is a more usual 37 ppm (free ligand values 146.7 and 105.0 ppm;[36] coordinated ligand values 40.2 and 68.0 ppm for the chromium derivative and 48.5 and 65.2 ppm for the molybdenum analogue, respectively[31]). This reversal in order is quite remarkable. Noting the absence of tetrahedral distortion at the methylene carbon atom C(15), we ascribe this large coordination shift to shielding effects.

Formation of the Complex. The complex forms rapidly in solution and appears to be quite inert with respect to rearrangement to the endo isomer. Both the cyclic and semicyclic double bonds appear to be equally available for coordination, so that stabilization of the exo product relative to the endo isomer through steric factors can be discounted. But it is still unclear, whether the unusual and exclusive preference of Cr(CO)$_3$ and Mo(CO)$_3$ groups for exo coordination to ligand I is governed by steric kinetic factors or whether electronic thermodynamic factors are important.

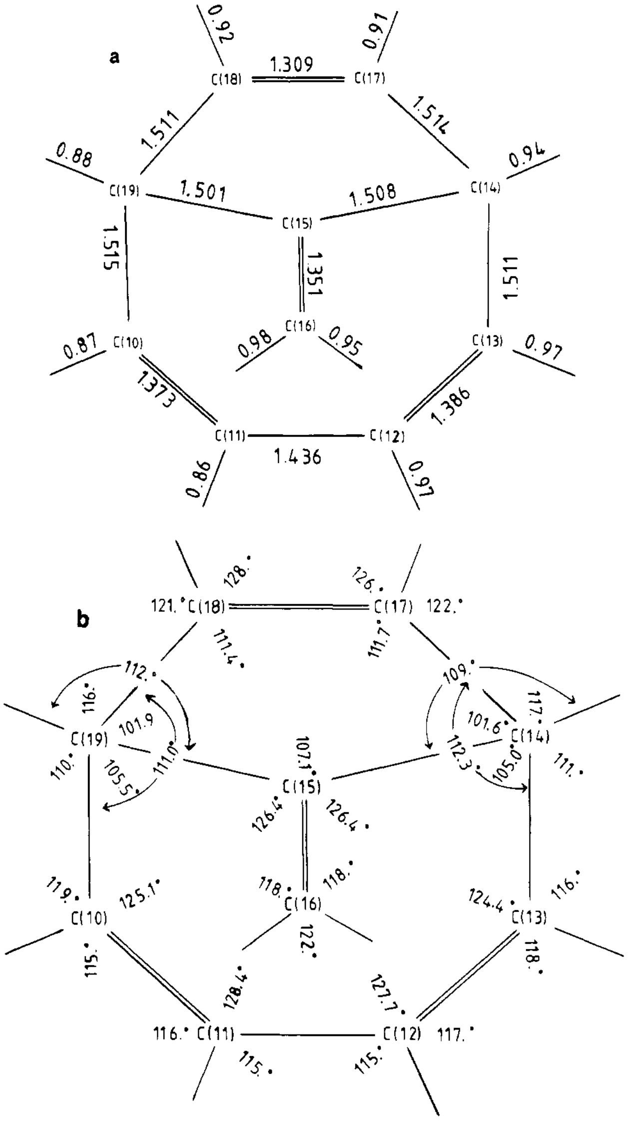

Figure 4. Bond distances (a) and bond angles (b) in the ligand I.

Simple-minded considerations of olefinic π and π* orbital overlap with metal d orbitals yield no clues to electronic factors involved. However, plausible steric kinetic factors exist. It is reasonable to assume, given the strained nature of ligand I, that the observed conformation of the ligand, when coordinated, closely resembles its uncoordinated conformation. Furthermore, given the trienophilic nature of the Cr(CO)$_3$ and Mo(CO)$_3$ species, interaction of these with the butadiene moiety probably dominates in the transition state. Approach of the $Cr(CO)_3$ group toward the butadiene moiety is rather *less* hindered on the exo side than on the endo side—the dihedral angle between the butadiene plane and the cyclic double bond C(17)–C(18) (plane Ene 2) is only 87.5°, while the dihedral angle made with the coordinated semicyclic olefin is 116.3° (as seen by an approaching $Cr(CO)_3$ group, see also Figure 3 and Table VIII). In addition, at distances where the Cr–butadiene interaction is weak, interaction with the terminal methylene carbon atom is possible. Thus, for certain directions of approach, the methylene semicyclic double bond could serve to guide the approaching $Cr(CO)_3$ group toward the butadiene component, thereby further enhancing exo approach.

Comparison with Other $M(CO)_3$(triene) Species. Among structurally characterized complexes containing the $Cr(CO)_3$ or $Mo(CO)_3$ moiety, it is only rarely that two carbonyl lgands approach trans geometry and then only as a result of coordination of the central atom to a phosphine ligand and a diolefin.[16,18] In other cases,[3-15,17,19-24] particularly among the more precisely determined structures, deviations of the C_{CO}–Cr–C_{CO} bond angles from 90° are small. It should be noted that these angles generally average to a value less than 90°, presumably from the steric demands of the olefinic or other ligands. Thus, the C(1)–Cr–C(2) angle, which we have observed, is one of the largest found, while the average angle of 87.8° is entirely normal. While some apparently significantly short Cr–C_{CO} bonds are known, these are invariably in structures of low precision; for example, a Cr–C_{CO} bond of 1.72 (2) Å is associated with a C–O separation of 1.27 (2) Å.[23] Among the conjugated triene complexes the values observed here for the Cr–C_{CO} bonds are entirely comparable.

The Cr—$C_{C=C}$ bonds lie comfortably within the range which has been observed for triene and diene complexes, although it is only in the curious homoaromatic systems[11-13] that bonds longer than the 2.386 (3) Å for the Cr—C(16) bond determined here have been found.

As noted earlier, butadiene–olefin and triolefin complexes are exceedingly scarce and only the $Mo(CO)_3$(5,6-dimethylenebicyclo[2.2.1]hept-2-ene) complex is available for comparison. Here there is an angle of ~60° between the olefin plane and the butadiene plane.

Concluding Remarks. Studies on appropriately substituted derivatives of I with extension to molybdenum and tungsten tricarbonyl complexes are planned, in order to probe further the binding properties of this ligand and equally important the coordinating properties of the $M(CO)_3$ species.

Acknowledgment. We gratefully acknowledge Professor H. R. Oswald and the Swiss National Science Foundation for the use of X-ray diffraction facilities and for financial support.

Registry No. $Cr(CO)_3(CH_3CN)_3$, 16800-46-7; $Cr(CO)_3(C_{10}H_{10})$, 70585-10-3.

Supplementary Material Available: A table of thermal parameters (Table III) and a listing of structure amplitudes (Table IV) (9 pages). Ordering information is given on any current masthead page.

Labilization of CO Dissociation from Metal Clusters. 2. An Investigation of Substitution Reactions of Bissubstituted Derivatives of Tetrairidium Dodecacarbonyl, $Ir_4(CO)_{10}L_2$ (L = PPh_3, $P(OPh)_3$, PBu_3, and $AsPh_3$)

David C. Sonnenberger and Jim D. Atwood*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received December 3, 1981

The reactions of $Ir_4(CO)_{10}L_2$ with an additional ligand have been studied for L = PPh_3, $P(OPh)_3$, $AsPh_3$, and PBu_3. Good pseudo-first-order kinetics were observed for each cluster, and the activation parameters were evaluated for each reaction. The primary reaction pathway involves CO dissociation from the cluster in the rate-determining step. Examination of the rates of CO loss from the series of complexes $Ir_4(CO)_{10}L_2$, L = PPh_3, $P(OPh)_3$, $AsPh_3$, PBu_3, and CO, reveals a dramatic labilization in the order CO < $P(OPh)_3$ < PBu_3 < PPh_3 ≤ $AsPh_3$. These ligands span 3 orders of magnitude in the CO dissociation rate. It is proposed that CO dissociation occurs at a substituted metal center with bridging carbonyls transferring the coordinative unsaturation to a second unsubstituted center. The kinetic labilization by the presence of the substituent ligand L arises from a stabilization of the transition state.

Introduction

In an earlier paper dealing with the substitution processes of $Ir_4(CO)_{11}L$, we reported a significant enhancement in the rate of CO dissociation from the monosubstituted clusters, as compared to the parent cluster, $Ir_4(CO)_{12}$.[1] The degree of acceleration in the rate of CO loss varied with the nature of the substituent ligand

$$CO < P(OPh)_3 < AsPh_3 < PPh_3 < PBu_3 \qquad (1)$$

This labilization of CO loss was ascribed to a stabilization of the resulting transition state by the presence of the substituent ligand. This phenomenon is not unique to the tetrairidium carbonyl clusters; CO dissociation was 55 times more rapid from $Ru_3(CO)_{11}PPh_3$ than from $Ru_3(CO)_{12}$.[2]

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[1] Sonnenberger, D. C.; Atwood, J. D. *J. Am. Chem. Soc.*, in press.

[2] Malik, S. K.; Poë, A. *Inorg. Chem.* 1978, *17*, 1484.