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Iron, Molybdenum and Tungsten Carbonyls of 5,6,7,8-Tetrakis(methylene)bicyclo-[2.2.2]oct-2-ene. Crystal and Molecular Structure of $(C_{12}H_{12})Fe(CO)_3$*

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*The reaction of 5,6,7,8-tetrakis(methylene)bicyclo-[2.2.2]oct-2-ene (1) with $Fe_2(CO)_9$ yields under various conditions the exo and endo-tetrahaptotricarbonyliron complexes (2 and 3) and the endo, exo-bis(tetrahaptotricarbonyliron) complex (4); with $Fe(CO)_3$(benzalacetone), 2 and the bis(exo-tetrahapto-tricarbonyliron) complex (5) are obtained. The title ligand reacts with $M(CO)_3(CH_3CN)_3$ (M = Mo, W) giving respectively the hexahapto-tricarbonylmolybdenum and -tungsten complex (6, 7). Coordination of all five double bonds of the pentaene is achieved by reacting 2 with $Mo(CO)_3(CH_3CN)_3$ giving the exo-tetrahapto-tricarbonyliron-hexahapto-tricarbonylmolybdenum complex (8). The structures of complexes 3–8 in solution were deduced from their NMR data and the molecular structure of 2 was determined by X-ray crystallography. The $Fe(CO)_3$ group is in the exo position with respect to the roof-shaped pentaene. The ligand is bound through one s-*cis*-*butadiene group to two basal positions of a tetragonal pyramidal $Fe(CO)_3X_2$ moiety. Hydrogen atom positions were refined in the last cycles (final residual R = 0.023). H(Z) atoms deviate from the diene plane of the coordinated diene away from the metal by ~42°, whereas H(E) atoms deviate towards the metal by ~16°. Hybridization at the "inner" carbon atoms as well as at the carbon atoms of the other three double bonds does not differ significantly from sp^2.*

A kinetic study of the cycloaddition reaction of a dienophile to the free 1,3-diene system of the monometallic complexes shows that the rate with respect to that of the free ligand is not much affected by the presence of the metal.

Introduction

5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (*1*) is a new pentaene [2] bearing one endocyclic double bond and two exocyclic s-*cis*-butadiene groups. Its coordination to Fe(0) or Mo(0) would block selectively two, three or four double bonds and leave the remaining ones free for cycloaddition reactions [3]. With this goal in mind, we have synthesized its various iron, molybdenum and tungsten tricarbonyl complexes and report here on their spectroscopic properties, their geometry in solution as well as a crystal structure determination of one isomer of $(C_{12}H_{12})Fe(CO)_3$ and a kinetic study of the cycloaddition of a dienophile to the monometallic complexes.

Reactions of *1* with Fe, Mo and W Carbonyls

Iron carbonyls may form at least four complexes with 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (*1*): the exo- and endo-tetrahapto-tricarbonyliron isomers (*2* and *3*) and the endo, exo- and bis-(exo)-bis(tetrahapto-tricarbonyliron) isomers (*4* and *5*).

Irradiation of *1* at –80 °C in pentane in the presence of $Fe(CO)_5$ in excess gives complex *2* with a low yield (6%) as polymerization of the ligand occurs. Reacting *1* with $Fe_2(CO)_9$ in n-hexane gives *2* with a higher yield (31%)*, together with the endo-

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*For a preliminary account, see ref. [1].

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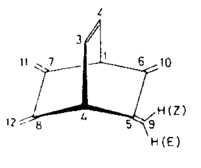
*The optimization of yields was not attempted.

TABLE I. Summary of Crystal Data, Intensity Collection, and Refinement.

Formula	$(C_{12}H_{12})Fe(CO)_3$ $C_{15}H_{12}O_3Fe$	Radiation	Mo-K_α, Nb filtered $\lambda = 0.71069$ Å
Mol. weight	296.1	μ, cm^{-1}	11.6
Dimensions, mm	0.18 × 0.20 × 0.24	Scan method	2θ–θ
Crystal system	Triclinic	Background from	Scan profile interpretation [4]
a, Å	6.9803(8)	$(\sin\theta/\lambda)_{max}$	0.54
b, Å	9.8398(8)	Data collected	$h, k, l > 0$
c, Å	10.4034(10)	No. of unique reflections	1770
α, deg	108.480(7)	No. of reflections $< 3\sigma$	127
β, deg	98.814(8)	No. of observations/No. of variables	8
γ, deg	91.028(8)		
V, $Å^3$	668.0(1)	Structure solution	Patterson and Fourier
Z	2	Refinement method	Block diagonal least-squares
d_{calcd}, g/cm^3	1.47	Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
d_{obsd}, g/cm^3	1.45(1)	w	$1/\sigma^2$
F_{000}	304	R	0.023
Space group	$P\bar{1}$	R_w	0.029
		Goodness of fit	2.63



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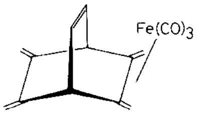

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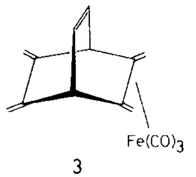

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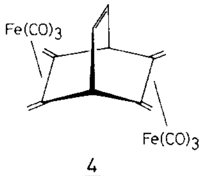

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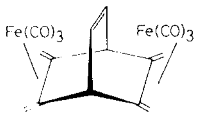

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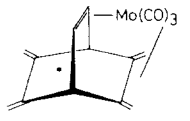

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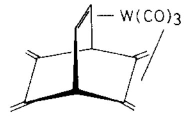

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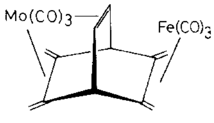

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isomer *3* (29%) and the endo, exodiiron complex *4* (8%); decreasing the ratio *1*: $Fe_2(CO)_9$ increases the yield of *4* (51%). Reacting *1* with $Fe(CO)_3$(bza) (bza = benzalacetone) gives *2* (31%) and the bis(exo)-diiron complex *5* (7%). *5* can also be obtained by displacing benzalacetone from $Fe(CO)_3$(bza) in benzene by the free s-*cis*-butadiene group of complex *2* (40% yield). The hexahapto-tricarbonylmolybdenum complex *6* and its tungsten analog *7* are the sole products of the reaction of *1* with $M(CO)_3(CH_3CN)_3$ (M = Mo or W) in ether. Coordination of all five carbon–carbon double bonds is obtained by reacting *2* with $Mo(CO)_3(CH_3CN)_3$ in ether which yields the exo-tetrahapto-tricarbonyl-iron-hexahapto-tricarbonyl-molybdenum complex *8*. Blocking of two, three, four or five double bonds can thus be achieved with the desired configuration, except that corresponding to the bis(endo)-bis(tetrahapto-tricarbonyliron) complex which cannot be formed for steric reasons as shown by molecular models.

The crystal and molecular structure of *2* has been determined to serve as a reference for the assignments of the spectroscopic data of all complexes.

Crystal Structure of $(C_{12}H_{12})Fe(CO)_3$, 2

X-Ray measurements were carried out with a Syntex $P2_1$ automatic diffractometer. The methods used and results obtained are summarized in Table I.

The intensities of the check reflections decreased by about 30% during the period of measurements and the measured intensities were corrected accordingly. A numerical absorption correction was applied to the intensities, using a crystal form accurately measured as before [5]. The computer programs used for the data reduction and structure analysis were taken

TABLE II. Atomic Coordinates and Thermal Parameters (the e.s.d. of the last significant digit is given in parentheses). The temperature factor has the form e^{-T} where $T = 2\pi^2 \Sigma h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic atoms and $T = 8\pi^2 U \sin^2 \theta/\lambda^2$ for isotropic atoms.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.0919(4)	0.1442(2)	0.3350(2)	0.051(2)	0.041(1)	0.045(1)	−0.001(1)	0.019(1)	0.011(1)
C(2)	0.2626(5)	0.2151(3)	0.4455(2)	0.080(2)	0.042(1)	0.032(1)	−0.010(1)	0.013(1)	0.005(1)
C(3)	0.4334(5)	0.1791(3)	0.4141(2)	0.062(2)	0.049(1)	0.038(1)	−0.012(2)	−0.009(2)	0.016(1)
C(4)	0.4278(4)	0.0739(2)	0.2716(2)	0.042(2)	0.041(1)	0.041(1)	0.007(1)	0.004(1)	0.015(1)
C(5)	0.3048(3)	0.1303(2)	0.1669(2)	0.043(2)	0.025(1)	0.032(1)	0.002(1)	0.006(1)	0.0066(8)
C(6)	0.1222(4)	0.1670(2)	0.2004(2)	0.042(2)	0.029(1)	0.036(1)	−0.003(1)	0.004(1)	0.0069(9)
C(7)	0.1113(4)	−0.0180(2)	0.3043(2)	0.059(2)	0.040(1)	0.031(1)	−0.005(1)	0.004(1)	0.0139(9)
C(8)	0.3033(4)	−0.0582(2)	0.2652(2)	0.062(2)	0.037(1)	0.031(1)	0.004(1)	0.002(1)	0.0143(9)
C(9)	0.3553(5)	0.1483(2)	0.0460(2)	0.054(2)	0.037(1)	0.041(1)	0.007(1)	0.013(1)	0.012(1)
C(10)	−0.0069(4)	0.2201(3)	0.1107(3)	0.042(2)	0.042(1)	0.058(2)	0.004(1)	0.006(1)	0.016(1)
C(11)	−0.0274(5)	−0.1049(3)	0.3147(3)	0.068(2)	0.055(2)	0.062(2)	−0.008(2)	0.010(2)	0.025(1)
C(12)	0.3628(6)	−0.1902(3)	0.2262(3)	0.085(3)	0.047(2)	0.064(2)	0.011(2)	0.018(2)	0.026(1)
C(13)	0.1701(4)	0.4737(2)	0.3041(2)	0.052(2)	0.034(1)	0.056(1)	0.002(1)	0.014(1)	0.015(1)
C(14)	0.2339(4)	0.4133(2)	0.0360(2)	0.069(2)	0.040(2)	0.059(1)	0.010(1)	0.017(1)	0.018(1)
C(15)	0.5067(4)	0.4043(2)	0.2541(2)	0.054(2)	0.040(1)	0.054(1)	−0.003(1)	0.017(1)	0.005(1)
Fe(1)	0.26383(5)	0.34003(3)	0.17340(3)	0.0449(2)	0.0299(1)	0.0413(2)	0.0038(2)	0.0106(2)	0.0114(1)
O(1)	0.1118(3)	0.5610(2)	0.3886(2)	0.081(2)	0.050(1)	0.075(1)	0.013(1)	0.032(1)	0.0054(9)
O(2)	0.2166(4)	0.4557(2)	−0.0556(2)	0.135(2)	0.083(1)	0.074(1)	0.020(1)	0.024(1)	0.052(1)
O(3)	0.6624(3)	0.4444(2)	0.3067(2)	0.057(2)	0.085(1)	0.088(1)	−0.015(1)	0.008(1)	0.005(1)
H(1)	−0.032(4)	0.170(2)	0.358(2)	0.038(6)					
H(2)	0.243(4)	0.277(2)	0.523(2)	0.060(8)					
H(3)	0.553(4)	0.210(2)	0.465(2)	0.052(7)					
H(4)	0.555(3)	0.052(2)	0.250(2)	0.038(6)					
H(9E)	0.485(4)	0.149(2)	0.036(2)	0.047(7)					
H(9Z)	0.257(4)	0.118(2)	−0.033(2)	0.044(7)					
H(10E)	−0.106(4)	0.264(2)	0.147(2)	0.051(8)					
H(10Z)	−0.013(4)	0.177(3)	0.016(3)	0.065(8)					
H(11E)	−0.143(4)	−0.072(3)	0.343(2)	0.056(8)					
H(11Z)	−0.010(5)	−0.210(3)	0.292(3)	0.080(9)					
H(12E)	0.493(4)	−0.212(3)	0.203(3)	0.069(9)					
H(12Z)	0.277(5)	−0.272(3)	0.221(2)	0.077(9)					

from the 'X-RAY 72' program system [6]. Scattering factors for the neutral atoms were taken from Cromer [9]. The structure was solved by Patterson and Fourier methods. All hydrogen atoms were found after prior refinement to R = 0.052. The final structure was refined to R = 0.023. Positional and thermal parameters for all the atoms are listed in Table II. Calculated bond lengths and angles are reported in Table III and IV, respectively. The equations for several least-squares planes and some dihedral angles are presented in Table V. A view of the molecular structure, obtained with the program ORTEP [10], is given in Fig. 1, where the numbering scheme is indicated. For the $C_{12}H_{12}$ moiety, the numbering scheme is identical with that used for nomenclature purposes.

Discussion

The structure is composed of discrete monomeric $(C_{12}H_{12})Fe(CO)_3$ molecules.

TABLE III. Bond Lengths (A) in *2* (the e.s.d. of the last significant digit is given in parentheses).

Fe–C(5)	2.069(2)	C(2)–C(3)	1.309(5)
Fe–C(6)	2.069(2)	C(13)–O(1)	1.149(3)
Fe–C(9)	2.107(2)	C(14)–O(2)	1.147(3)
Fe–C(10)	2.108(3)	C(15)–O(3)	1.141(4)
Fe–C(13)	1.782(2)		
Fe–C(14)	1.781(3)	Fe–C(15)	1.780(3)
C(1)–C(2)	1.507(4)	C(3)–C(4)	1.510(3)
C(1)–C(6)	1.531(4)	C(4)–C(5)	1.532(3)
C(1)–C(7)	1.538(3)	C(4)–C(8)	1.528(4)
C(1)–H(1)	0.95(3)	C(4)–H(4)	0.96(2)
C(2)–H(2)	0.88(2)	C(3)–H(3)	0.91(2)
C(11)–H(11E)	0.93(3)	C(12)–H(12E)	0.99(3)
C(11)–H(11Z)	1.00(3)	C(12)–H(12Z)	0.97(3)
C(5)–C(9)	1.418(4)	C(6)–C(10)	1.423(4)
C(5)–C(6)	1.396(4)	C(7)–C(8)	1.484(4)
C(9)–H(9E)	0.93(3)	C(10)–H(10E)	0.90(3)
C(9)–H(9Z)	0.95(2)	C(10)–H(10Z)	0.93(3)
C(7)–C(11)	1.320(4)	C(8)–C(12)	1.327(4)

TABLE IV. Bond Angles (°) in *2* (the e.s.d. of the last significant digit is given in parentheses).

C(5)–Fe–C(9)	39.7(1)	C(13)–Fe–C(14)	102.0(1)
C(5)–Fe–C(6)	39.4(1)	C(13)–Fe–C(15)	91.1(1)
C(6)–Fe–C(10)	39.8(1)	C(14)–Fe–C(15)	101.3(1)
C(2)–C(1)–C(6)	109.3(2)	C(3)–C(4)–C(5)	109.2(2)
C(2)–C(1)–C(7)	105.0(2)	C(3)–C(4)–C(8)	105.9(2)
C(6)–C(1)–C(7)	102.9(2)	C(5)–C(4)–C(8)	102.5(2)
H(1)–C(1)–C(2)	115(1)	H(4)–C(4)–C(3)	113(1)
H(1)–C(1)–C(6)	112(1)	H(4)–C(4)–C(5)	113(1)
H(1)–C(1)–C(7)	111(1)	H(4)–C(4)–C(8)	113(1)
C(1)–C(2)–C(3)	115.2(2)	C(2)–C(3)–C(4)	114.5(2)
H(2)–C(2)–C(1)	120(2)	H(3)–C(3)–C(4)	117(2)
H(2)–C(2)–C(3)	125(2)	H(3)–C(3)–C(2)	129(2)
C(4)–C(5)–C(9)	128.1(2)	C(1)–C(6)–C(10)	129.0(2)
C(4)–C(5)–C(6)	112.8(2)	C(1)–C(6)–C(5)	112.6(2)
C(6)–C(5)–C(9)	119.1(2)	C(5)–C(6)–C(10)	118.4(2)
C(1)–C(7)–C(11)	122.6(3)	C(4)–C(8)–C(12)	122.8(3)
C(1)–C(7)–C(8)	110.8(2)	C(4)–C(8)–C(7)	111.1(2)
C(8)–C(7)–C(11)	126.6(2)	C(7)–C(8)–C(12)	126.1(3)
H(9E)–C(9)–H(9Z)	120(2)	H(10E)–C(10)–H(10Z)	123(2)
H(9E)–C(9)–C(5)	119(2)	H(10E)–C(10)–C(6)	114(2)
H(9Z)–C(9)–C(5)	116(2)	H(10Z)–C(10)–C(6)	118(2)
H(11E)–C(11)–H(11Z)	118(3)	H(12E)–C(12)–H(12Z)	117(2)
H(11E)–C(11)–C(7)	122(2)	H(12E)–C(12)–C(8)	123(2)
H(11Z)–C(11)–C(7)	120(2)	H(12Z)–C(12)–C(8)	120(2)
Fe–C(13)–O(1)	179.1(2)	Fe–C(15)–O(3)	179.1(3)
Fe–C(14)–O(2)	177.4(2)		

TABLE V. Least-squares Planes for *2*.

Plane	Atom defining plane[a]	Equation of mean plane
I	C(1), C(2), C(3), C(4)	0.636X + 9.099Y − 6.779Z = −0.899
II	C(1), C(4), C(5), C(6)	1.989X + 7.911Y + 1.851Z = 1.941
III	C(1), C(4), C(7), C(8)	1.482X − 1.736Y + 9.592Z = 3.105
IV	C(7), C(8), C(11), C(12)	1.706X − 1.859Y + 9.484Z = 3.125
V	C(5), C(6), C(9), C(10)	1.919X + 7.897Y + 1.949Z = 1.942
VI	C(13), C(15), a, b	0.448X − 5.553Y + 9.785Z = 0.444
VII	Fe, C(14), O(2), c, d, e[b]	6.680X − 2.092Y − 2.964Z = 0.603

Displacement of atoms from mean plane (Å)

Plane I	C(1) − 0.002	Plane II	C(1) + 0.003	Plane III	C(1) − 0.006
	C(2) + 0.003		C(4) − 0.003		C(4) + 0.006
	C(3) − 0.003		C(5) + 0.005		C(7) + 0.010
	C(4) + 0.002		C(6) − 0.005		C(8) − 0.010
Plane IV	C(7) − 0.016	Plane V	C(5) − 0.002	Plane VI	C(13) − 0.023
	C(8) + 0.016		C(6) + 0.002		C(15) + 0.023
	C(11) + 0.008		C(9) + 0.001		a − 0.029
	C(12) − 0.008		C(10) − 0.001		b + 0.029
					(Fe − 0.518)
Plane VII	Fe − 0.066	c − 0.032			
	C(14) − 0.012	d + 0.036			
	O(2) + 0.055	e + 0.018			

Dihedral angle between planes (°)

I–II	126.0;	I–III	119.5;	II–V	179.3;	III–IV	178.0;	V–VI	89.6;		
I–VII	89.1;	II–VII	89.8;	III–VII	88.3;	IV–VII	86.2;	V–VII	89.7;		
VI–VII	89.7.										

[a] a, b, c, d and e are the midpoints of the C(5)–C(9), C(6)–C(10), C(5)–C(6), C(2)–C(3) and C(7)–C(8), respectively. [b] The differences between the distances of equivalent atoms from the plane lie between 0.01 and 0.19 Å.

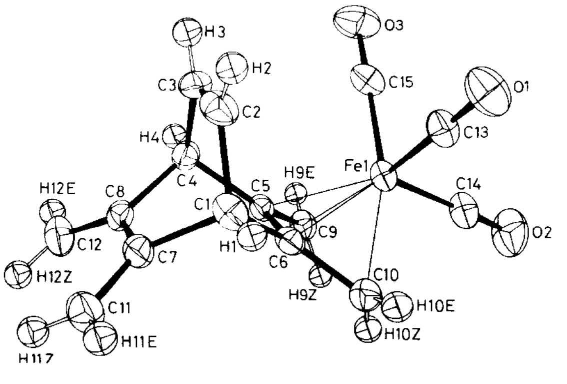


Fig. 1. A perspective view of the molecular structure of $(C_{12}H_{12})Fe(CO)_3$ (*2*).

There is essentially mirror symmetry for the whole molecule, with the mirror plane VII (Table V) passing through the Fe atom, one CO group and the midpoints of the bonds C(2)–C(3), C(5)–C(6) and C(7)–C(8). The $Fe(CO)_3$ group is in the 'exo' position with respect to the roof-shaped ligand. The arrangement of ligands about the iron atom is approximately tetragonal pyramidal. Four coordination sites are occupied by 2CO and the midpoints a and b of the exo C–C bonds of one s-*cis*-butadiene system, a-b-C(13)–C(15) defining the basal plane (Table V). The apex-to-base angles are 102° for the carbonyl groups and 112° for the C–C bond midpoints. The basal angles are 91, 92 and 64°, the small angle being that subtended by the two outer C–C bonds of the diene. The diene is perpendicular to the basal plane and the Fe atom lies 0.5 Å over it. The apical Fe–CO bond makes an angle of 8° with the normal to the basal plane.

The difference in bond distances between the weighted average of Fe–C(9) and Fe–C(10) and the weighted average of Fe–C(5) and Fe–C(6) is 0.038(2) Å. Significantly longer Fe–C distances are thus formed for the terminal carbon atoms of the diene than for the 'inner' ones. The difference between C(5)–C(6) and the weighted average of C(5)–C(9) and C(6)–C(10) is 0.025(4) Å. It should however be noted that a statistical comparison of 41 structures of

TABLE VI. ^{1}H and ^{13}C Spectra of Iron, Molybdenum and Tungsten Carbonyl Complexes of *1*.[a]

	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*
H(1), H(4)[g]	3.84 dd	3.97 (dd, −0.13)[b]	4.08 (dd, −0.24)	4.33 (dd, −0.49)	4.24 (dd, −0.40)	3.39 (dd, 0.45)	3.40 (m, 0.44)	3.42 (dd, 0.42)
H(2), H(3)	6.34 dd	6.48 (dd, −0.14)	6.78 (dd, −0.44)	7.03 (dd, −0.69)	6.82 (dd, −0.48)	3.66 (dd, 2.68)		3.75 (dd, 2.59)
H(9E), H(10E)	4.92 bs	2.12 (d, 2.80)	1.92 (d, 3.00)	2.22 (dd, 2.70)	2.31 (d, 2.61)	3.49 (d, 1.43)	3.42 (d, 1.50)	2.17 (d, 2.75)
H(11E), H(12E)		5.15 (s, −0.23)	4.84 (s, 0.08)	2.26 (dd, 2.66)		5.03 (s, −0.11)	5.08 (s, −0.16)	3.55 (d, 1.37)
H(9Z), H(10Z)	5.21 s	0.54 (d, 4.67)	0.17 (d, 5.04)	0.52 (d, 4.69)	0.59 (d, 4.62)	1.56 (d, 3.65)	1.36 (d, 3.85)	0.71 (d, 4.50)
H(11Z), H(12Z)		5.43 (s, −0.22)	5.15 (s, 0.06)	0.66 (d, 4.55)		5.40 (s, −0.19)	5.44 (s, −0.23)	1.83 (d, 3.38)
^{3}J H(1)–H(2)[c]	4.5	4.6	4.4	4.4	4.4	4.3		4.4
^{4}J H(1)–H(3)	3.3	3.3	3.1	3.0	3.4	2.8		2.8
$\|^2J\|$ H(9E)–H(9Z)	<0.5	2.6	2.4	2.8	2.7	1.3	1.9	2.7
$\|^2J\|$ H(11E)–H(11Z)		<0.5	<0.5	3.0		<0.5	<0.5	1.6
C(1), C(4)	53.2 d	50.1 (d, 3.1)	51.1 (d, 2.1)	49.1 (d, 4.1)	48.7 (d, 4.5)	46.2 (d, 7.0)	46.1 (d, 7.1)	43.5 (d, 9.7)
C(2), C(3)	132.2 d	134.6 (d, −2.4)	136.5 (d, −4.3)	140.2 (d, −8.0)	139.0 (d, −6.8)	54.0 (d, 78.2)	41.1 (d, 91.1)	52.8 (d, 79.4)
C(5), C(6)	144.9 s	108.4 (s, 36.5)	112.7 (s, 32.2)	113.3 (s, 31.6)	113.3 (s, 31.6)	83.0 (s, 61.9)	77.1 (s, 67.8)	110.7 (s, 34.2)
C(7), C(8)		143.7 (s, 1.2)	144.9 (s, 0)	111.4 (s, 33.5)		143.6 (s, 1.3)	146.5 (s, −1.6)	84.4 (s, 60.5)
C(9), C(10)	103.9 t	40.2 (t, 63.7)	35.8 (t, 68.1)	41.0 (t, 62.9)	50.6 (t, 63.3)	64.9 (t, 39.0)	58.4 (t, 45.5)	40.7 (t, 63.2)
C(11), C(12)		105.8 (t, −1.9)	102.6 (t, 1.3)	38.8 (t, 65.1)		105.8 (t, −1.9)	105.9 (t, −2.0)	65.1 (t, 38.8)
CO	–	211.6 s	211.6 s	211.4 s	211.4 s	218.8 s[e] 228.9 s[e]	209.2 s[e] 222.1 s[e]	210.9 s[f] 228.0 s[e] 216.9 s[e]
^{1}J C(1)–H(1)	144 ± 3	140 ± 2	142 ± 2	140 ± 3	136 ± 4	141 ± 2	142 ± 2	141 ± 3
^{1}J C(2)–H(2)	170 ± 1	174 ± 1	175 ± 1	176 ± 2	170 ± 2	172 ± 1	176 ± 2	175 ± 3
^{1}J C(9)–H(9)	158 ± 1	157 ± 1	161 ± 1	159 ± 1	160 ± 1	165 ± 1	162 ± 2	160 ± 1
^{1}J C(11)–H(11)		159 ± 1	160 ± 1	160 ± 1		159 ± 1	159 ± 1	163 ± 2

[a] In CD_2Cl_2 at room temperature. [b] δ (in ppm relative to TMS); in parentheses: multiplicity and $\Delta\delta = \delta$(ligand − δ(complex); s: singlet, bs: broad singlet, d: doublet, t: triplet, m: multiplet. [c] Coupling constants in Hz. [d] Line widths at half-height of proton signals decrease in the sequence H(E) > H(1) > H(Z) > H(2); H(Z) protons were assumed to couple significantly only with H(E) protons. [e] Intensity ratio lower field signal/higher field signal is ½. [f] Fe–CO; exchange blocked at −40 °C: δ = 208.7 (2CO) and 214.6 ppm (1CO). [g] The numbering scheme and the coordination position of the metal atoms are indicated in Figure 1.

TABLE VII. Second-order Rate Constant for the Cycloaddition of DMA to the Pentaene *1*, the Tetraene *14* and to Their Monometallic Complexes in CCl_4 at 50 °C.[a]

Substrate	$k_2 \times 10^4\ M^{-1}\ s^{-1}$	Substrate	$k_2 \times 10^4\ M^{-1}\ s^{-1}$
Pentaene ligand (*1*)	13.1	Tetraene ligand (*14*)	48
monoadduct of *1* (*10*)	5.6	monoadduct of *14* (*18*)	48
exo-$Fe(CO)_3$ complex (*2*)	2.1	exo-$Fe(CO)_3$ complex (*15*)	16
endo-$Fe(CO)_3$ complex (*3*)	2.3	endo-$Fe(CO)_3$ complex (*16*)	26
exo-$Ru(CO)_3$ complex (*9*)	1.6	endo-$Ru(CO)_3$ complex (*17*)	25

[a] As measured by ^1H NMR spectroscopy (see Experimental).

the type (1,3-diene)$Fe(CO)_3$ gives a difference of 0.013(16) Å [11]. On the average, the three C–C distances have then to be considered of equal lengths. The terminal C–C averaged distances are 1.421(3) and 1.324(4) Å for the bonded and the free diene group respectively. The corresponding 'inner' C–C distances are 1.396(4) and 1.484(4) Å. Complexation causes thus the terminal C–C bonds to become longer by 0.097(4), whereas the 'inner' C–C bond becomes shorter by 0.088(6) Å. The free butadiene system is strictly planar (including the hydrogen atoms). In contrast, H(Z) atoms deviate from the bonded diene plane away from the metal by 42° and H(E) atoms deviate towards the metal by 16°. These values are in agreement with the mean deviations of 42(4) and 14(3)° found from a statistical comparison of 7 (1,3-diene)$Fe(CO)_3$ structures unsubstituted at the terminal carbons [11].

Spectroscopic Properties

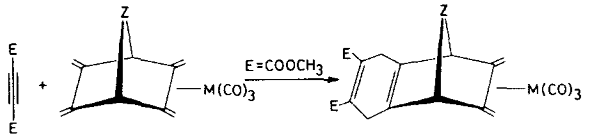
The ^1H and ^{13}C NMR spectral data of ligand *1* and its Fe, Mo and W complexes are reported in Table VI and their IR and mass spectral data in the experimental part. The assignments of the NMR spectra were deduced from the multiplicity of the signals, by comparison of $\Delta\delta = \delta(\text{ligand } 1) - \delta(\text{complex})$ with the corresponding values for the diene 2,3-dimethylenebicyclo[2.2.2]octane and the triene 5,6-dimethylenebicyclo[2.2.2]oct-2-ene and their tricarbonyliron complexes [12].

The NMR spectra of *2* and *3* show resonances attributable to three uncoordinated C–C double bonds. However, the different positions of the iron atoms do not affect the H(2, 3) chemical shifts significantly enough to decide which isomer is the exo one in solution. For this reason we assumed that the geometry of complex *2* is the same in solution as in the solid state. This assumption is based on the observation that *2* and *3* (and also *3* and *4*) did not epimerize either by heating their solution in toluene up to the boiling point or by adding a trace of acid (HCl) to their solution in benzene or chloroalkanes. Complex *5*, the main product of the reaction between *2* and $Fe(CO)_3$(bza), must be the bis(exo) isomer as the magnetic equivalence of C(1, 4) and that of C(5, 6, 7, 8) require C_{2v} symmetry with two mirror planes defined respectively by C(1), C(2), C(3), C(4) and by the midpoints of bonds C(5)–C(6), C(2)–C(3), C(7)–C(8). Complex *4* must then be the endo, exo-diiron isomer as the non-equivalence of C(5, 6) and C(7, 8) implies the loss of one mirror plane (the geometry of *4* has been further confirmed by a crystal structure determination [13]). The Mo or W atom is bonded in the exo position to the apical C–C double bond in *6*, *7* and *8* as the H(2, 3) and C(2, 3) signals experience a large upfield shift. As *8* is derived from *2*, the iron atom must also be located at the exo position in this complex. The relative intensities of the fragmentation peaks found in the mass spectra of tricarbonyliron complexes of some bicyclic trienes were used by Hansen *et al.* [12] to distinguish between exo- and endo-isomers. They found that the intensity of the (M^+–CO) peak of tetrahapto-5,6-bis(methylene)bicyclo[2.2.2]oct-2-ene-endo-tricarbonyliron, the displacement of one CO by the free C–C isomer. They attributed this observation to the formation in the gas phase of the ion hexahapto-5,6-bis(methylene)bicyclo[2.2.2]oct-2-ene-endo-tricarbonyl iron, the displacement of one CO by the free C–C double bond being possible only in the endo complex. In the present case, this intramolecular displacement should occur for *2* but not for *3*. However, no difference was found in their mass spectra, thus Hansen's method seems to be of limited applicability.

Diels–Alder Reactivity of the Monocomplexes

Chemical and spectroscopic properties of the s-*cis*-butadiene function in 2,3-bis(methylene)norbornane can be modified by remote substitution of the bicyclic skeleton [14]. Thus, it appeared of interest to determine whether an homoconjugaged diene–$Fe(CO)_3$ or diene–$Ru(CO)_3$ group could affect the chemical properties of the free diene in the monocomplexes of *1* and of related systems. The rates of the cycloadditions of dimethylacetylenecarboxylate (DMA) to the pentaene *1*, to the tetraene 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane (*14*) and to their corresponding tetrahapto-$Fe(CO)_3$ and

-Ru(CO)$_3$ complexes have been evaluated (see Table VII).



Z = CH=CH	M = Fe(exo)	*1*	*10*
	M = Fe(endo)	*2*	*11*
	M = Ru(exo)	*3*	*12*
		9	*13*
Z = CH$_2$–CH$_2$	M = Fe(exo)	*14*	*18*
	M = Fe(endo)	*15*	*19*
	M = Ru(endo)	*16*	*20*
		17	*21*

Monocomplexation by Fe(CO)$_3$ or Ru(CO)$_3$ of the tetraene *14* leads to rate retardations of the Diels–Alder additions of the free diene in the monocomplexes *15, 16, 17* compared with *14*. The rate retardation effects were about equal to the statistical factor introduced by removal of one diene function in the ligand *14*. Somewhat larger rate retardation effects were observed with the complexes *2, 3* and *9* compared with the addition of DMA to the pentane *1*. Unfortunately, these effects are too small to justify any discussion about the possible factors responsible for the observed changes in the Diels–Alder reactivity of these systems. It is interesting to note, however, that the reactivity of the free diene in the complexes *2, 3, 9* and *15, 16, 17* is apparently independent upon the stereochemistry (exo *vs.* endo), and the metal (Fe *vs.* Ru). The rates of cycloadditions of the Mo(CO)$_3$ and W(CO)$_3$ complexes *6* and *7* to strong dienophiles (DMA, tetracyanoethylene) could not be measured as these complexes were rapidly decomposed in presence of these reagents. Coordination of DMA by the Mo and W was found to be faster than its cycloaddition to the free diene in *6* and *7*, respectively (see experimental part) and resulted in the catalytic cyclotrimerisation of DMA. Catalysis of such trimerisations by other complexes have been reported [15].

Experimental

All reactions were carried out in an atmosphere of argon and the solvents were purified, dried and degassed by standard methods [16]; Mass spectra at 70 eV were measured with a Hewlett-Packard GC-MS 5980; UV spectra in isooctane with a Beckman Acta V spectrophotometer; IR spectra in n-hexane with a Perkin-Elmer 577 spectrophotometer; ^{1}H (60 MHz) and ^{13}C (15.08 MHz; spectrum width: 3750 Hz, 4096 points) NMR spectra with a Bruker WP-60 spectrometer in the FT mode and using a deuterium lock. E. Manzer (Mikrolabor, ETH Zürich) carried out the microanalyses.

The preparation of 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (*1*) has been described elsewhere [2].

Reaction of 1 *with Fe, Mo and W Carbonyls*

a) Fe$_2$(CO)$_9$ (6.5 g) and *1* (2 g) were stirred at room temperature in n-hexane (400 ml) for 2 days. Acid alumina, activity grade I was then added to decompose the Fe$_3$(CO)$_{12}$ formed. After filtration and removal of solvent, the residue was taken up in n-hexane and chromatographed on a 70 X 2 cm column packed with Florisil using n-hexane as eluent. The successive fractions of eluate yielded after recrystallisation from n-pentane at –25 °C the complexes *2* (31%), *3* (29%) and *4* (8%). Overall yield 68%. The same reaction in ether/pentane under reflux gives a lower yield of complexes consisting mainly of *2* (22%). Heating under reflux Fe$_2$(CO)$_9$ (15 g) and *1* (2 g) in 300 ml n-hexane for 3 days yields as main product the endo, exo isomer *4* (51%), together with *2* + *3* (9%) and a trace of *5*. Overall yield 60%.

2: pale yellow crystals; m.p. 109–110 °C. *Anal.* Found. C, 60.81; H, 4.02; $C_{15}H_{12}O_3Fe$ Calcd.: C, 60.85; H, 4.09%. Mass spectrum: 296 (1; M$^+$), 268 (39; M$^+$–CO), 240 (76; M$^+$–2CO), 212 (100; M$^+$–3CO), 56 (28; Fe$^+$). IR spectrum: ν(CO) 2063 (A′(1)), 1984 (A′(2)) and 1973 cm^{-1} (A″ (assigned following Adams [17]). UV spectrum: λ_{max} in nm (ϵ in 1 mol^{-1} cm^{-1}): 294 sh (4067), 262 sh (9152), 250 sh (12880), 222 (25700). The free ligand absorbs at 269 sh (5320), 260 (8850), 252 (9030), 236 (9650), 227.5 (10150), 221 (9400).

3: yellow crystals; m.p. 68–69 °C. *Anal.* Found: C, 60.93; H, 4.08; $C_{15}H_{12}O_3Fe$ Calcd: C, 60.85; H 4.09%. Mass spectrum: 296 (2; M$^+$), 268 (34; M$^+$–CO), 240 (67; M$^+$–2CO), 212 (100; M$^+$–3CO), 156 (20), 56 (41). IR spectrum: ν(CO) 2060, 1982 and 1975 cm^{-1}. UV spectrum: 292 sh (2812), 259 sh (5940), 250 sh (8360), 219 (19000).

4: yellow crystals; m.p. 142 °C. *Anal.* Found: C, 49.70; H, 2.87; $C_{18}H_{12}O_6Fe_2$ Calcd.: C, 49.59; H, 2.77%. Mass spectrum: 436 (0.1; M$^+$), 408 (20; M$^+$–CO), 380 (36; M$^+$–2CO), 352 (33; M$^+$–3CO), 324 (8; M$^+$–4CO), 296 (75; M$^+$–5CO) 268 (100; M$^+$ –6CO), 56 (70). IR spectrum: ν(CO) 2059, 1986 and 1973 cm^{-1}. UV spectrum: 228 sh (5680), 221 (32900).

b) Fe(CO)$_3$(benzalacetone) [18] (0.2 g) and *2* (0.14 g) were heated at 60 °C in benzene (60 ml) for 2 days. After filtration and removal of solvent, the residue was taken up in n-hexane and chromatographed on a 40 X 2 cm column packed with Florisil using n-hexane as eluent. After recrystallisation from n-pentane at –25 °C, the first fraction of eluate yielded complex *5* (40%) and *4* (9%).

5:yellow crystals; m.p. 165 – 166 °C. *Anal.* Found: C, 50.99; H, 3.08; $C_{18}H_{12}O_6Fe_2$ Calcd.: C, 49.59; H, 2.77%. Mass spectrum: 436 (0.7; M$^+$), 408 (63;

M^+–CO), 380 (90; M^+–2CO), 352 (76; M^+–3CO), 324 (13; M^+–4CO), 296 (66; M^+–5CO), 268 (100; M^+–6CO), 112 (10), 56 (20). IR spectrum: 2058, 1985 and 1972 cm^{-1}. UV spectrum: 328 sh (4280), 221 (34000).

c) $Fe(CO)_5$ (8.78 g) and *1* (0.7 g) were irradiated in n-pentane (200 ml) at –80 °C for 4 h (high pressure Hg lamp HPK 125; pyrex vessel). After evaporation to a small volume, the reaction mixture was chromatographed on a 80 × 2 cm column packed with Florisil using n-hexane as eluent. This preparation gave only a small yield of *2* (6%) after recrystallisation. $Fe_2(CO)_9$ formed during the irradiation and the ligand was mainly polymerized.

d) $Mo(CO)_3(CH_3CN)_3$ [19] (1 g) and *1* (0.4 g) were heated under reflux in dry and degassed diethyl ether (200 ml) for 16 h and then evaporated to dryness. The brownish residue was taken up in ether, filtered and chromatographed on a 25 × 2 cm column packed with Florisil. Elution with ether/hexane (1:9) revealed only one red band which yielded *6* (46%) after recrystallisation in n-pentane at –25 °C.

6: red crystals unstable in the air; m.p. 118–130 °C (dec.). *Anal.* Found: C, 54.27; H, 3.70; $C_{15}H_{12}O_3Mo$ Calcd.: C, 53.59; H, 3.60%. Mass spectrum (peaks corresponding to ^{96}Mo): 336 (21; M^+), 308 (15; M^+–CO), 280 (13; M^+–2CO), 252 (69; M^+–3CO), 156 (100). IR spectrum: ν(CO) 1994, 1935 and 1908 cm^{-1}. UV spectrum: 356 sh (7690), 333 (11150), 267 sh (10080), 229 (28500), 219 (32300).

e) A solution of $W(CO)_6$ (2 g) in acetonitrile (150 ml) was refluxed for 2 days. After distilling the solvent off, $W(CO)_3(CH_3CN)_3$ and the unreacted $W(CO)_6$ were taken up in ether/benzene (1:1 ;200 ml) containing *1* (0.41 g). The reaction mixture was heated under reflux for 4 days and then evaporated to dryness. The residue was taken up in hexane and chromatographed on a 25 × 2 cm column packed with Florisil. Elution with n-hexane (95%)/ether (5%) revealed only one red band which yielded *7* contaminated with $W(CO)_6$ (350 mg). *7* was purified by fractional sublimation and recrystallized from n-pentane at –25 °C (25%).

7: deep red crystal unstable in the air; m.p. 142–144 °C. *Anal.* Found: C, 42.97; H, 2.90; $C_{15}H_{12}O_3W$ Calcd.: C, 42.48; H, 2.85%. Mass spectrum (peaks corresponding to ^{184}W): 424 (50; M^+), 396 (19; M^+–CO), 368 (25; M^+–2CO), 340 (100; M^+–3CO), 184 (3), 156 (14). IR spectrum: ν(CO) 1994, 1938 and 1902 cm^{-1}. UV spectrum: 350 sh (6097), 326 (10200), 268 (8290), 223 (29000).

f) A solution of $Mo(CO)_6$ (1 g) in acetonitrile (120 ml) was refluxed for 6 h. After distilling the solvent off, the residue was taken up in diethylether (200 ml) containing *2* (0.42 g). The reaction mixture was heated under reflux for 21 h and then evaporated to dryness. The residue was taken up in hexane/ether and chromatographed on a 70 × 2 cm column packed with Florisil using ether (30%)/n-hexane (70%) as eluent. The orange eluate containing *8* and $Mo(CO)_6$ was evaporated to dryness and the solid product purified by fractional sublimation. The residue was recrystallized from n-pentane at –25 °C yielding *8* (58%).

8: orange crystals; m.p. 140–142 °C. *Anal.* Found: C, 45.64; H, 2.59; $C_{18}H_{12}O_6MoFe$ Calcd.: C, 45.41; H, 2.54%. Mass spectrum (peaks corresponding to ^{96}Mo): 476 (27; M^+), 448 (11; M^+–CO), 420 (20; M^+–2CO), 392 (23; M^+–3CO), 364 (15; M^+–4CO), 336 (13; M^+ –5CO), 308 (48; M^+–6CO), 212 (100), 156 (15), 56 (35; Fe^+). IR spectrum: ν(CO) of $Fe(CO)_3$ 2062, 1999 and 1978 cm^{-1}; ν(CO) of $Mo(CO)_3$ 1990, 1942 and 1912 cm^{-1}.

Cycloaddition of Dimethylacetylenedicarboxylate (DMA) to the Free Diene Group of the Monometallic Complexes

a) A solution of *2* (0.24 g) and DMA (0.59 g) in benzene (25 ml) was heated at 50 °C for 28 h. The solvent was distilled off and the waxy product pumped off at 10^{-3} torr for 2 h. Recrystallization from ether/n-pentane at –25 °C yielded the adduct *11* (97%).

11,12-bis(methylene-4,5-dimethoxycarbonyl-$\Delta^{2,7}$-tricyclo[6.2.2.$0^{2,7}$]dodeca-2,4,9-triene-exo-tricarbonyliron (*11*): pale yellow crystals stable in the air; m.p. 167–169 °C. *Anal.* Found: C, 57.42; H, 4.17; $C_{21}H_{18}O_7Fe$ Calcd.: C, 57.62; H, 4.14%. Mass spectrum: 438 (~0.5; M^+), 410 (3; M^+–CO), 382 (13; M^+–2CO), 354 (32; M^+–3CO), 300 (8), 270 (14), 242 (22), 210 (18), 59 (100), 56 (21; Fe^+). IR spectrum: ν(CO) 2059, 1979 and 1968 cm^{-1}, ν(COOMe) 1742 and 1735 cm^{-1}. UV spectrum: 298 sh (3225), 230 sh (19350), 217 (23800). ^1H NMR data (in CD_2Cl_2 at room temperature); δ in ppm *vs.* TMS (multiplicity; coupling constant in Hz): H(1,8) 4.19 (dd; 3.3 and 4.2), H(3, 6) 3.30(bs), H(9, 10) 6.72(dd), H(11′(E), 12′(E)) 2.17 (d; 2.8), H(11′(Z), 12′(Z)) 0.47(d), CH_3 3.74(s). ^{13}C NMR data (same conditions): C(1, 8) 50.4 (d; 137), C(2, 7) 132.9(s), C(3, 6) 30.9 (t; 133), C(4, 5) 139.1(s), C(4′,5′) 168.2(s), C(9, 10) 137.7 (d; 172), C(11, 12) 114.1(s), C(11′, 12′) 40.1 (t; 156, CH_3 52.4 (q; 145), CO 211.4(s).

b) A solution of 3 (0.41 g) and DMA (0.98 g) in benzene (30 ml) was heated at 50 °C for 27 h. The solvent was distilled off and the residue was chromatographed on a 10 × 1 cm column packed with Florisil using benzene as eluent. After recrystallisation from ether-pentane at –25 °C, the first fraction of eluate yielded the adduct *12* (71%).

11,12-bis(methylene)-4,5-dimethoxycarbonyl-$\Delta^{2,7}$-tricyclo[6.2.2.$0^{2,7}$]dodeca-2,4,9-triene-endo-tricarbonyliron (*12*): pale yellow crystals stable in the air; m.p. 130–132 °C. *Anal.* Found: C, 57.50; H, 4.18; $C_{21}H_{18}O_7Fe$ Calcd.: C, 57.56; H, 4.14%. Mass spectrum: 438 (1; M^+), 410 (4; M^+–CO), 382 (2; M^+–2CO), 354 (68; M^+–3CO), 326 (20), 296 (16), 264 (11), 236 (67), 184 (80), 178 (76), 128 (75), 127 (78), 56 (100; Fe^+). IR spectrum: ν(CO) 2058, 1979 and 1965 cm^{-1}, ν(COOMe) 1741 and 1734 cm^{-1}. UV spectrum: 292 (2880), 238 sh (6570), 219 (9960). ^1H NMR data: H(1, 8) 4.25 (dd; 2.9 and 4.1), H(3,6), 3.23 (d; 0.9), H(9, 10) 6.99 (dd), H(11′(E), 12′(E)) 2.15 (d; 2.5), H(11′(Z), 12′(Z)) 0.40 (d), CH_3 3.71 (s).

c) A solution of tetrahapto-5,6,7,8-tetrakis-(methylene)bicyclo[2.2.2]oct-2-ene-exo-tricarbonylruthenium $(C_{12}H_{12})Ru(CO)_3$ (*9*) [13] (0.15 g) and DMA (0.115 g) in CCl_4 (12 ml) was heated at 45 °C for 17 h. The solvent was distilled off and the remaining oil pumped off at 10^{-3} torr for 2 h. The residue was taken up in benzene and chromatographed on a 6 X 1 cm column packed with Florisil using benzene as eluent. After recrystallisation from ether/n-pentane, the first fraction of eluate yielded the adduct *13* (64%).

11,12-bis(methylene)-4,5-dimethoxycarbonyl-$\Delta^{2,7}$-tricyclo-[6.2.2.$0^{2,7}$]dodeca-2,4,9-triene-exo-tricarbonylruthenium (*13*): white crystals; m.p. 112–115 °C. *Anal.* Found: C, 52.38; H, 3.74; $C_{21}H_{18}O_7Ru$ Calcd.: C, 52.18; H, 3.75%. Mass spectrum (peaks corresponding to ^{101}Ru): 455 (53; M^+–CO), 427 (34; M^+–2CO), 399 (100; M^+–3CO). IR spectrum: ν(CO) 2070 (A′(1)), 1991 (A′(2)) and 1980 cm^{-1} (A″), ν(COOMe) 1741 and 1732 cm^{-1}. UV spectrum: 304 (2010, 222 (15600). ^1H NMR data: H(1, 8) 4.17 (dd; 3.2 and 4.2), H(3, 6) 3.28 (d; 1.1), H(9, 10) 6.60 (dd), H(11′(E), 12′(E)) 2.20 (d; 2.8), H(11′(Z), 12′(Z)) 0.69 (d). CH_3 3.74(s). ^{13}C NMR data: C(1, 8) 51.2 (d; 144), C(2, 7) 133.2(s), C(3, 6) 31.1 (t; 131), C(4, 5) 138.5(s), C(4′,5′) 168.5(s), C(9, 10) 138.5 (d; 167), C(11, 12) 117.4(s), C(11′,12′) 33.4 (t; 157), CH_3 52.3 (q; 145), CO 196.1(s) and 201.4(s) (the intramolecular CO exchange is blocked at room temperature).

d) Cycloaddition of DMA was also attempted on the free diene group of the Mo and W complexes (*6*, *7*) under the same conditions as for *2*, but extensive decomposition of the complex occurred. The reaction was then carried out on a vacuum line by distilling deutero-toluene in a NMR tube containing *6* and DMA (1:3) and warming the sealed tube to 0 °C. The solution turned brownish and its ^1H NMR spectrum showed that the characteristic pattern of the H(2, 3) proton of *6* (doublet of doublet at 3.66 ppm, J = 2.6 and 4.3 Hz) was shifted downfield to 6.35 ppm (dd; 3.3 and 4.5 Hz). This signal corresponds to the H(2, 3) resonance of the free apical double bond of the pentaene (*cf.* Table VI). It indicates that the first site of attack by DMA is at the molybdenum atom and not at the free diene group. Prolonged stirring of the solution resulted in the decomposition of the complex. Only a white product exempt of molybdenum was isolated from the reaction mixture: m.p. 187–188 °C. Mass spectrum: 426 (2; M^+), 395 (100), 364 (6), 349 (11), 293 (7), 220 (8), 139 (31); $\delta(CH_3)$ 3.8 ppm (18H with respect to toluene as reference); ν(COOMe) 1742 cm^{-1}. The melting point and the other data correspond to those of hexamethoxycarbonylbenzene [20]. Thus complex *6* catalyses the cyclotrimerisation of DMA.

e) Kinetic Measurements. The same technique was used to measure the rate of cycloaddition of DMA to the pentaene *1*, its monometallic complexes *2*, *3* and η^4-$(C_{12}H_{12})$ exo-Ru(CO)$_3$ (*9*) [13]), to the related tetraene 2,3,5,6-tetrakis(methylene)bicyclo-[2.2.2]octane $C_{12}H_{14}$ (*14*) and its monometallic complexes η^4-$(C_{12}H_{14})$exo-Fe(CO)$_3$ (*15*), -endo-Fe-(CO)$_3$ (*16*) and -endo-Ru(CO)$_3$ (*17*) (the preparation of the tetraene complexes is described elsewhere [11]).

A typical procedure is described below for complex *2*: CCl_4 (0.53 ml) was distilled on a vacuum line into an NMR tube containing *2* (30.1 mg), DMA (14.1 mg), toluene (8.7 mg) and a sealed capillary containing C_6D_{12} for the deuterium lock, The tube was thermostatted at 50 °C and the ^1H NMR spectrum was recorded periodically with a Bruker WP-60 in the FT mode (10 scans at 50 ± 2 °C) until the reaction was 80% complete. The relative concentrations of *2*, DMA and the adduct were determined with respect to each other and to a fixed concentration of toluene as reference from the observed integrals of the H(11, 12) signals of *2* and the H(methyl) peaks of DMA and the adduct. It was thus demonstrated that the only reaction taking place is the cycloaddition for which the rate constant was derived from the equation $1/(a - b) \ln a(a - x)/b(b - x) = k_2t$ (a, b: initial concentrations mol/l; x: $[\mathit{11}]_t$; the density of the solution was taken into account to calculate these concentrations).

The identity of the product was confirmed by comparison of the spectrum with that of an authentic sample of *11*.

The ^1H NMR data of the tetraene *14* and its complexes *15*, *16* and η^4-$(C_{12}H_{14})$ exo-Ru(CO)$_3$ *17* are reported elsewhere [11], those of *10*, *18* in [14]. The corresponding DMA adducts, similar to *11*, *12*, *13* were identified by their ^1H NMR data given below.

19: tetrahapto-9,10-bis(methylene)-4,5-dimethoxycarbonyl-$\Delta^{2,7}$-tricyclo[6.2.2.$0^{2,7}$]dodeca-2,4-diene-exo-tricarbonyliron, η^4-$(C_{18}H_{20}O_4)$exo-Fe(CO)$_3$; H(1,8) 3.32 (bs 2H), H(3,6) 3.27 (bs 4H), H(9′(E), 10′(E)) 1.81 (d 2H; 2.6), H(9′(Z), 10′(Z)) 0.12 (d 2H), H(11, 12) 1.8 (m 4H), CH_3 3.74 (s 6H).

20: η^4-$(C_{18}H_{20}O_4)$ endo-Fe(CO)$_3$; H(1,8) 3.21 (bs 2H), H(3,6) 3.12 (bs 4H), H(9′(E), 10′(E)) 1.98 (d 2H; 2.4), H(9′(Z), 10′(Z)) 0.33 (d 2H), H(11, 12) 1.81 (bs 4H), CH_3 3.73 (s 6H).

η^4-($C_{18}H_{20}O_4$)endo-Ru(CO)$_3$ (*21*): H(1, 8) 3.19 (bs 2H), H(3, 6) 3.10 (bs 4H), H(9′(E), 10′(E)) 2.04 (d 2H; 2.7), H(9′(Z), 10′(Z)) 0.58 (d 2H), H(11, 12) 1.86 (bs 4H), CH_3 3.74 (s 6H).

Dehydrogenation of Adduct 11

Aromatisation of the carbocycle of *11* bearing the two dimethoxycarbonyl groups was attempted using the method of Schiess and Heitzmann [21] for the dehydrogenation of the tris-DMA adduct of hexakis-(bromomethyl)benzene. Under the conditions used, aromatisation was not complete and was accompanied by partial or total decomplexation of iron:

a) *11* (0.030 g) and the catalyst C/Pd (10%) (0.013 g) were heated at 50 °C in methanol (6 ml) for two weeks. The solvent was distilled off and the residue extracted with diethylether yielding a solid mixture (24 mg; overall yield 85%) of unreacted *11* (22%), the aromatized complex *22* (65%) and two organic compounds *10* (8%) and *23* (5%) identified by their ^{1}H NMR spectra.

22: 11,12-bis(methylene)-4,5-dimethoxycarbonyl-tricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9-tetraene-tricarbonyliron; H(1, 8) 4.72 (dd 2H; 3.3 and 4.2), H(3, 6) 7.66 (s 2H), H(9, 10) 6.88 (dd 2H), H(11′(E), 12′(E)) 2.22 (d 2H; 2.8), H(11′(Z), 12′(Z)) 0.47 (d 2H), CH_3 3.85 (s 6H); IR spectrum: ν(CO) 2058, 1978 and 1967 cm^{-1}, ν(COOMe) 1742 cm^{-1}.

b) *11* (0.033 g) and C/Pd(10%) (0.165 g) were heated under reflux in toluene (12 ml) for 22 h. The solvent was distilled off and the residue extracted with n-pentane, then ether. After recrystallisation from n-pentane at –25 °C, a white product exempt of iron was obtained (12 mg; 54%) consisting of *10* (28%) and *23* (72%).

10: H(1, 8) 3.8 (m 2H), H(3, 6) 3.1 (bs 4H), H(9, 10) 6.4 (m 2H), H(11′(E), 12′(E)) 4.8 (s 2H), H(11′(Z), 12′(Z)) 5.0 (s 2H), CH_3 3.72 (s 6H); ν(COOMe) 1741 cm^{-1}. These data correspond to those of 11,12-bis(methylene)-4,5-dimethoxy-carbonyl-$\Delta^{2,7}$-tricyclo[6.2.2.0^{2,7}]dodeca-2,4,9-triene [14].

23: H(1, 8) 4.61 (dd 2H; 3.0 and 4.2), H(3, 6) 7.56 (s 2H), H(9, 10) 6.61 (dd 2H), H(11′(E), 12′(E)) 5.06 (s 2H), H(11′(Z), 12′(Z)) 5.26 (s 2H), CH_3 3.84 (s 6H); ν(COOMe) 1742 cm^{-1}. These data compared with those of *22* and *10* indicate that *23* is the benzoderivative 11,12-bis(methylene)-4,5-dimethoxycarbonyltricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9-tetraene.

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