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STEREOSELECTIVE OXIDATION OF RUTHENIUM AND IRON CARBONYL COMPLEXES OF 5,6,7,8-TETRAKIS(METHYLENE)BICYCLO[2.2.2]OCT-2-ENE

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Summary

The reaction of the pentaene 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (I) with $Ru_3(CO)_{12}$ under various conditions yields *exo*- and *endo*-tetrahaptotricarbonylruthenium complexes (IIa and IIIa). Mixed d^8 bimetallic complexes were obtained by the reaction of the *exo*-$Fe(CO)_3$ complex IIb with $Ru_3(CO)_{12}$, giving the *exo*-$Fe(CO)_3$, *exo*-$Ru(CO)_3$ (VI) and *exo*-$Fe(CO)_3$, *endo*-$Ru(CO)_3$ (VII) isomers. The same reaction starting with the *endo*-$Fe(CO)_3$ complex IIIb gave the third isomer *endo*-$Fe(CO)_3$, *exo*-$Ru(CO)_3$ (VIII). Metal substitution and intermolecular epimerisation occurs in the reaction of IIa with (benzalacetone)$Fe(CO)_3$ to give VII, VIII, and the *endo,exo*-bis(tricarbonylruthenium) complex (IVa), and with $Fe_2(CO)_9$ in excess to give IVb and the diexo-bis(tricarbonyliron) isomer Vb. Coordination of all five double bonds of I was achieved by the reaction of IIa with $W(CO)_3(CH_3CN)_3$ giving the *exo*-tetrahaptotricarbonylruthenium-hexahaptotricarbonyltungsten complex (IXa). Surprisingly, the oxidation of the bimetallic complexes with one equivalent Ce^{IV} was found to be stereoselective in certain cases. The oxidation of VII, VIII, and IVb removes exclusively the metal in the *exo* position. In contrast, no selectivity was found during the oxidation of VI and of the *endo,exo*-bis(tricarbonyliron) complex X of the parent tetraene 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane. In these systems the stereoselectivity of the oxidation is independent of the nature of the metal and occurs whenever stabilisation of the higher oxidation state of Ru or Fe can be achieved by transient coordination to the free endocyclic double bond of the ligand. The oxidation of the bimetallic complexes IXa (Ru—W) and IXb (Fe—Mo) with one equivalent Ce^{IV} removes the d^6 metal exclusively.

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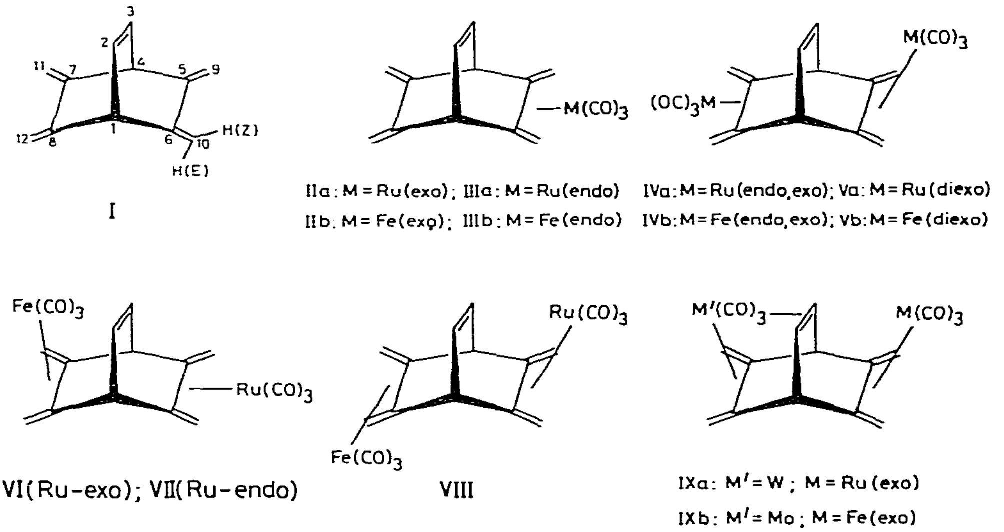
Introduction

5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene (I) is a pentaene [1] bearing one endocyclic double bond and two exocyclic *s-cis*-butadiene groups. Since the *exo* and *endo* faces with respect to the rigid roof-shaped skeleton are easily distinguishable, this compound is a model ligand for studying the role of the nature and the position of the metal on the behaviour of its complexes in reactions such as dienophile cycloadditions and electrophilic substitutions. We reported recently [2] the synthesis of various Fe, Mo and W tricarbonyl complexes of the title ligand, as well as a crystal structure determination of $(\eta^4\text{-}C_{12}H_{12})Fe(CO)_3(exo)$ IIb and a kinetic study of the cycloaddition of a dienophile to I and to the monometallic complexes. We report here the synthesis of the Ru complexes, some mixed d^8 and d^8, d^6 bimetallic complexes, their spectroscopic properties, their geometry in solution, and a study of the factors affecting the stereoselectivity of oxidation of bimetallic complexes.

Synthesis and spectroscopic properties of Ru, Ru—Fe and Ru—W complexes of I

The reaction of I with $Ru_3(CO)_{12}$ in refluxing toluene or methanol gives the $(\eta^4\text{-}1,3\text{-diene})Ru(CO)_3$ isomers (IIa: *exo*; IIIa: *endo*) in 28 and 6% yields, respectively (Scheme 1). The displacement of 1,5-cyclooctadiene by I from (cod)$Ru(CO)_3$ [4] did not occur under these conditions or upon irradiation in n-pentane at —70 or 0°C. In contrast with the complexation of I by iron carbonyls [2], no *endo,exo*-bis(tetrahaptotricarbonylruthenium) complex (IVa) nor the di*exo* isomer Va was formed by the direct reaction of I with $Ru(CO)_{12}$. This is probably due to the low "$Ru(CO)_4$"/ligand I ratio obtained in refluxing toluene and to a statistical factor favouring the coordination of "$Ru(CO)_4$" to I (which has two 1,3-diene groups) with respect to IIa or IIIa (which have only

SCHEME 1



one free diene group). However, IVa was obtained by metal substitution (vide infra).

Blocking of the two *s-cis*-butadiene groups of I by different d^8 metals (Fe and Ru) should give three isomers: the *exo*-$Ru(CO)_3$, *exo*-$Fe(CO)_3$ (VI), *endo*-$Ru(CO)_3$, *exo*-$Fe(CO)_3$ (VII) and *exo*-$Ru(CO)_3$, *ends*-$Fe(CO)_3$ (VIII) complexes. (A di*endo* complex cannot be formed for steric reasons as shown by the crystal structure determination of $(\eta^4\text{-}C_{12}H_{14})Fe(CO)_3$(*endo*) [3].) These compounds were obtained in two steps. The *exo*- and *endo*-$(\eta^4$-1,3-diene$)Fe(CO)_3$ complexes (IIb and IIIb) were first obtained by treating I with $Fe_2(CO)_9$ in n-hexane and separated by chromatography [2]. Then, reaction of the *exo*-$Fe(CO)_3$ isomer IIb with $Ru_3(CO)_{12}$ in refluxing toluene yielded VI (7%) and VII (39%). Likewise, the reaction of the *endo*-$Fe(CO)_3$ complex IIIb with $Ru_3(CO)_{12}$ in refluxing toluene or methanol yielded VIII (45%). Monitoring of the reaction by IR and ^1H NMR did not show any displacement of Fe by Ru, the rather low yields being due solely to a slow decomposition of the starting material at the high temperatures necessary to break the metal—metal bonds of the triruthenium cluster. In contrast, displacement of Ru by Fe was observed in attempts to synthesise the mixed bimetallic complexes starting with a Ru complex under homo- or heterogeneous conditions. The reaction of IIa with (benzalacetone)-$Fe(CO)_3$ [5] in benzene yielded VIII (9%) as expected, but also VII (16%) and the *endo,exo*-bis(tetrahaptotricarbonylruthenium) complex IVa (9%). These three products are probably formed by two parallel processes. The substitution of benzalacetone (bza) from (bza)$Fe(CO)_3$ by the free 1,3-diene group of IIa forms VIII. The displacement of $Ru(CO)_3$ by $Fe(CO)_3$ in IIa gives the *exo*-$Fe(CO)_3$ complex IIb and (bza)$Ru(CO)_3$ as intermediates. Benzalacetone is then displaced by the free 1,3-diene group of IIa and IIb giving IVa and VII, respectively. Since this reaction is too complex to be monitored, the following experiments were carried out to confirm the proposed steps. The direct reaction of (bza)$Fe(CO)_3$ with IIb (Fe-*exo*) complex in benzene yields the di*exo* complex Vb and the *endo,exo*-bis(tricarbonyliron) isomer IVb (40 and 9%), respectively, and free benzalacetone (50%), showing that the free diene group of a monometallated complex of I is indeed able to displace bza from (bza)Fe-$(CO)_3$. The thermal equilibrium IIa $\rightleftharpoons$ IIIa, IIb $\rightleftharpoons$ IIIb and VI $\rightleftharpoons$ VII $\rightleftharpoons$ VIII did not take place in solution when the complexes were heated in benzene in the presence or absence of traces of $Fe_2(CO)_9$, $Fe(CO)_5$, $Ru_3(CO)_{12}$ or (bza)Fe-$(CO)_3$. This rules out intramolecular epimerisation and shows that migration of the $Ru(CO)_3$ group in the reaction of IIa with (bza)$Fe(CO)_3$ must result from a metal substitution process. The same reaction with $Fe_2(CO)_9$ in excess in n-hexane removes $Ru(CO)_3$ from its complex to give $Ru_3(CO)_{12}$, the di*exo* complex Vb, and the *endo,exo*-bis(tricarbonyliron) isomer IVb (32%).

Coordination of all five double bonds of the pentaene requires a d^8 and a d^6 metal. Reaction of IIa with $W(CO)_3(CH_3CN)_3$ [6] in benzene gave the *exo*-tetrahaptotricarbonylruthenium-hexahaptotricarbonyltungsten complex IXa (29%) (no epimerisation was observed). A similar reaction was observed between IIb (Fe-*exo*) and $Mo(CO)_3(CH_3CN)_3$ giving the *exo*-tetrahaptotricarbonyliron-hexahaptotricarbonylmolybdenum complex IXb [2].

The ^1H and ^{13}C NMR spectral data for the Ru, Fe—Ru and Ru—W complexes of I are reported in Table 1 and the IR and mass spectral data in the experimental part.

TABLE 1

^{1}H AND ^{13}C NMR SPECTRAL DATA OF Ru, Ru—Fe AND Ru—W CARBONYLS OF I [a]

	I	IIa	IIIa	IVa	VI	VII	VIII	IXa
H(1,4) [b]	3,84 dd	3,89 dd	4.08 dd	4,28 dd	4,20 dd	4,28 dd	4,29 dd	3,29 s
H(2,3)	6,34 dd	6,35 dd	6.71 dd	6,82 dd	6,67 dd	6,94 dd	6,88 dd	3,31 s
H(9*E*,10*E*)	4,92 bs	2,12 d	1,98 d	2,26 d	2,35 d	2,24 d	2,27 d	2,23 d
H(9*Z*,10*Z*)	5,21 bs	0,74 d	0,41 d	0,80 d	0,82 d	0,73 d	0,91 d	0,97 d
H(11*E*,12*E*)	4,92	5.12 bs	4.81 bs	2,19 d	2,31 d	2,17 d	2,19 d	3,44 d
H(11*Z*,12*Z*)	5,21	5,40 bs	5.08 bs	0,72 d	0,58 d	0,57 d	0,50 d	1,67 d
^{3}J(H(1)—H(2))	4,5	4,6	4,3 '	4,6	4,4	4,2	4,1	<0,5
^{4}J(H(1)—H(3))	3,3	3,3	3,1	3,0	3,3	3,0	3,2	
^{2}J(H(9*E*)—H(9*Z*))	<0,5	2,9	3,0	3,0	3,2	3,1	3,3	3,2
^{2}J(H(11*E*)—H(11*Z*))	<0,5	<0,5	<0,5	3,0	2,5	2,7	2,6	1,9
C(1,4)	53,2 d	50,1 d	51,7 d		48,8 d	49,4 d	49,2 d	43,9 d
C(2,3)	132,2 d	135,2 d	135,9 d		138,5 d	139,3 d	139,0 d	40,1 d
C(5,6)	144,9 s	111,5 s	117,0 s		112,9 s	116,7 s	113;3 s	115,5 s
C(7,8)		143,6 s	146,4 s		111,7 s	112,1 s	111,4 s	80,4 s
C(9,10)	103,9 t	33,3 t	29,1 t		32,8 t	31,7 t	33,0 t	33,9 t
C(11,12)		106,0 t	102,2 t		40,8 t	40,2 t	39,7 t	58,9 t
CO	—	195,9 s	196,0 s		195,9, 201,8 *s*	195,9, 201,4 *s*	196,0, 201,7 s	196,1, 202,0
		201,8 s	201,9 s		211,3 s	211,2 s	211,1 s	210,2, 222,0
^{1}J(C(1)—H(1))	144 ± 3	140 ± 3	142 ± 2		146 ± 2	147 ± 1	145 ± 1	141 ± 2
^{1}J(C(2)—H(2))	170 ± 1	170 ± 1	173 ± 1		177 ± 1	176 ± 1	175 ± 1	175 ± 2
^{1}J(C(9)—H(9))	158 ± 1	161 ± 2	157 ± 2		160 ± 1	158 ± 1	160 ± 1	159 ± 1
^{1}J(C(11)—H(11))		160 ± 1	158 ± 2		162 ± 1	158 ± 1	158 ± 1	162 ± 1

[a] In CD_2Cl_2 at room temperature. [b] Chemical shifts in ppm, TMS as internal standard; s: singlet, bs: broad singlet, d: doublet, t: triplet. [c] Coupling constants in Hz. [d] Intensity ratio lower field signal/higher field signal is 1/2. [c] Fe—CO; exchange blocked at −40°C; δ(CO) 208.7 (2C) and 214.6 ppm (1C). [f] W—CO.

The assignments of the NMR spectra were deduced from the multiplicity of the signals, by comparison of $\Delta\delta = \delta$(ligand I) — δ(complex) with the corresponding values for the analogous iron complexes [2,3,7] and for the triene 5,6-bis(methylene)bicyclo[2.2.2]oct-2-ene and its tricarbonyliron complexes [8]. The NMR spectra of IIa and IIIa show resonances attributable to three uncoordinated C—C double bonds. The geometry of these monocomplexes is probably the same in solution as in the solid state, since they do not epimerise either upon heating their solutions in toluene to the boiling point or upon adding a trace of acid (HCl) to their solutions in benzene, ether, or chloroalkanes. The protons H(11, 12) are deshielded in IIa and shielded in IIIa with respect to those of the free ligand, indicating that IIIa is the *endo* isomer. The same effect was found for the corresponding tricarbonyliron complexes, where the geometry of the isomer (η^4-$C_{12}H_{12}$)Fe(CO)$_3$(*exo*) (IIb) was ascertained by a crystal structure determination [2]. Complex IVa must be the *endo,exo* bimetallic isomer because of the non-equivalence of the H_2C(9, 10) and H_2C(11, 12) groups (^1H and ^{13}C NMR). The distinction between the *s-cis*-butadiene systems bonded to Ru(CO)$_3$ and Fe(CO)$_3$ in VI, VII and VIII is based on selective proton irradiations and the comparison of ^2J H(*E*)—H(*Z*) coupling constants. This coupling constant is systematically greater for Ru (3.0—3.3 Hz) (see also [9]) than for Fe (2.4—2.7 Hz [2,3,7]). The ^{13}C NMR spectra of VII and VIII show that the intramolecular CO exchange in Ru(CO)$_3$ is blocked at room temperature (irrespective of its position), whereas that in Fe(CO)$_3$ has a lower activation energy (the two CO resonances having an intensity ratio lower field signal/higher field signal of $\frac{1}{2}$ appears only at ca. —40° C).

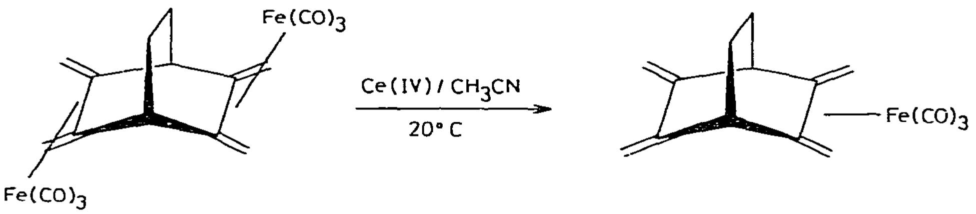
Oxidation of the bimetallic complexes

The removal of a M(CO)$_3$ group coordinated to a 1,3-diene is usually achieved by oxidising the metal with Ce^{IV} [10], a trialkylamine oxide [11] or CuCl$_2$/MeOH [12]. In the present case, the availability of several geometrical isomers having either two Fe atoms or one Fe and one Ru atom allow the study of the distribution of products under conditions chosen to oxidise about half of the metal content of the complexes. Surprisingly, the oxidation of the metal was found to be stereoselective for certain bimetallic complexes of the title ligand. The reaction of ($\eta^4 : \eta^4$-$C_{12}H_{12}$)Fe$_2$(CO)$_6$(*endo,exo*) (IVb [2]) with $(NH_4)_2[Ce(NO_3)_6]$ (molar ratio 1/2) in acetone at room temperature gave the *exo* and *endo* isomers IIb/IIIb and unreacted diiron complex IVb in the molar ratio 0.05/0.85/0.10. Complete disappearance of IVb occurs when using a molar ratio Ce^{IV}/complex = 2.8. The same monoiron isomers IIb/IIIb were obtained in the molar ratio 0.06/0.94 (yield 98%). This means that the products are stable under the conditions used to oxidise the diiron complex and that the observed molar ratio of products reflects a non-equivalent reactivity of the two Fe(CO)$_3$ groups.

The reaction of VIII (Fe-*endo*, Ru-*exo*) with $(NH_4)_2[Ce(NO_3)_6]$ (molar ratio 1/2) gave IIIb (Fe-*endo*) as the sole product (91%). Likewise, the reaction of VII (Fe-*exo*, Ru-*endo*) with Ce^{IV} (1/2) gave IIIa (Ru-*endo*) as the sole product. Thus, oxidation of these bimetallic complexes takes place preferentially at the *exo* position irrespective of the nature of the metal (Fe or Ru, which presumably have different normal redox potentials). This last point was confirmed by treating complex VI (having Fe and Ru both in the *exo* position) with Ce^{IV} (1/2). The products were IIa (Ru-*exo*) and IIb (Fe-*exo*) in the molar ratio 0.54/ 0.46.

The results suggest that preferential oxidation of the *exo* position is in some way due to the short contact distance between the endocyclic C(2)—C(3) double bond and the $M(CO)_3$ group (3.293(4) Å as shown by the crystal structure determination of $(\eta^4\text{-}C_{12}H_{12})Fe(CO)_3$(*exo*) IIb [2]). We thus looked at the product distribution of the oxidation of $(\eta^4 : \eta^4\text{-}C_{12}H_{14})Fe_2(CO)_6$(*endo,exo*) (X [3]), in which the organic ligand has a skeleton similar to that of I but without the endocyclic double bond. (Scheme 2). Its oxidation by Ce^{IV} or Me_3NO in acetone did not go to completion under the conditions used for the complexes of ligand I and partial decomposition of the formed monometallic complex liberated $C_{12}H_{14}$ which polymerised in the reaction mixture. However, its oxidation by Ce^{IV} in acetonitrile at room temperature gave a crystalline mixture of the *exo* and *endo* isomer $(\eta^4\text{-}C_{12}H_{14})Fe(CO)_3$ XI/XII in the molar ratio 0.59/ 0.41. Thus no selectivity was found in this case. Thus, we suggest that in these systems preferential oxidation of the metal in the *exo* position occurs whenever stabilisation of the higher oxidation state of Fe or Ru can be achieved by transient coordination to the free endocyclic double bond of the ligand.

SCHEME 2



X

XI : exo-Fe(CO)3

XII : endo-Fe(CO)3

Finally, the oxidation of IXa (η^4-$Ru(CO)_3$(*exo*), η^6-$W(CO)_3$) with one equivalent of Ce^{IV} in acetone yields exclusively IIa (Ru-*exo*). Likewise, the oxidation of IXb (η^4-$Fe(CO)_3$(*exo*), η^6-$Mo(CO)_3$) gives IIb as the sole product. Thus, the oxidation of half of the metal content of these d^8, d^6, bimetallic complexes preferentially removes the d^6 metal.

Experimental

All reactions were carried out under argon and the solvents were dried and degassed by standard methods [13]. 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; ^1H (60 MHz) and ^{13}C (15.08 MHz; spectral width 3700 Hz, 4096 points) NMR spectra with a Bruker WP-60 spectrometer operating in the FT mode and using a deuterium lock. E. Manzer (Microlabor, ETH Zürich) carried out the microanalyses.

The preparation of the following compounds has been described elsewhere: 5,6,7,8-tetrakis(methylene)bicyclo[2.2.2]oct-2-ene ($C_{12}H_{12}$, I) [1], (η^4-$C_{12}H_{12}$)-$Fe(CO)_3$ (IIb: *endo*; IIIb: *exo*), (η^4 : η^4-$C_{12}H_{12}$)$Fe_2(CO)_6$ (IVb: *endo,exo*; Vb di*exo*) [2], (η^4-$C_{12}H_{14}$)$Fe(CO)_3$ (XI: *exo*; XII: *endo*), (η^4 : η^4-$C_{12}H_{14}$)$Fe_2(CO)_6$ (X: *endo,exo*) ($C_{12}H_{14}$ = 2,3,5,6-tetrakis(methylene)bicyclo[2.2.2]octane) [3].

Reaction of I with ruthenium carbonyls

(a) $Ru_3(CO)_{12}$ (2.78 g, 4.35 mmol) and I (2.028 g, 13 mmol) were heated under reflux in methanol (400 ml) for 42 h. After filtration and removal of solvent, the residue was taken up in diethyl ether and chromatographed on a 12 × 2 cm column packed with Florisil using ether as eluent. The first fraction of eluate contained unreacted $Ru_3(CO)_{12}$. The second fraction was rechromatographed on a 70 × 2 cm column packed with Florisil using n-hexane as eluent which brought down a single yellow band. Fractional recrystallisations from n-pentane at —25°C gave IIa (1.238 g, 28%) and IIIa (0.254 g, 6%). No bis-(rutheniumtricarbonyl) complexes were observed.

IIa: Pale yellow air stable crystals. M.p. 93—94°C. Anal. Found: C, 52.93; H, 3.58. $C_{15}H_{12}O_3Ru$ calcd.: C, 52.78; H, 3.54%. Mass spectrum (peaks corresponding to ^{101}Ru): 341 (3; M^+), 313 (84; $M^+ - CO$), 285 (20; $M^+ - 2\ CO$), 257 (100; $M^+ - 3\ CO$), 101 (Ru^+). IR spectrum: $\nu(CO)$ 2077, 1996, 1986 cm^{-1}. UV spectrum, λ_{max} in nm (ϵ in M^{-1} cm^{-1}): 286 (4795), 257(sh) (8571), 246 (10650), 239 (10410), 214 (11840).

IIIa: pale yellow crystals. M.p. 63—65°C. Anal. Found: C, 52.85; H, 3.68. $C_{15}H_{12}O_3Ru$ calcd.: C, 52.78; H, 3.54%. Mass spectrum: 341 (12; M^+), 313 (71; $M^+ - CO$), 285 (73; $M^+ - 2\ CO$), 257 (100; $M^+ - 3\ CO$), 101 (Ru^+). IR: $\nu(CO)$ 2080, 1997, 1991 cm^{-1}. UV: 282 (2148), 259(sh) (3852), 247 (5222), 243(sh) (5110).

b) The same reaction in toluene (2.3 mmol $Ru_3(CO)_{12}$, 7 mmol I, 110°C, 22 h) gave IIa (30%) and IIIa (1%). These yields were not increased by increasing the ratio Ru/I.

c) The reaction of (cod)$Ru(CO)_3$ [4] (1.2 g, 4.1 mmol) with I (0.77 g, 4.9 mmol) in benzene (250 ml, 80°C, 20 h) resulted mainly in the polymerisation of I and formation of $Ru_3(CO)_{12}$.

Preparation of mixed bimetallic complexes

(a) (η^4-$C_{12}H_{12}$)$Fe(CO)_3$(*exo*) (IIb) (0.5 g, 1.69 mmol) and $Ru_3(CO)_{12}$ (0.8 g, 1.25 mmol) were heated at 110°C in toluene (85 ml) for 24 h. After filtration and removal of solvent, the residue was taken up in n-hexane/ether and chromatographed on a 35 × 2 cm column packed with Florisil. Elution with n-hexane/50 vol. % ether brought down a first band containing $Ru_3(CO)_{12}$ and a second band containing two complexes (as shown by TLC and ^1H NMR). Chromatography of the second fraction of eluate on a 40 × 2 cm column packed with Florisil using n-hexane as eluent followed by recrystallisation from n-pentane at —25°C gave complexes VI (0.065 g, 8%) and VII (0.316 g, 39%). The same reaction in methanol under reflux (1.4 mmol iron complex, 1.1 mmol $Ru_3(CO)_{12}$, 80 ml, 14 h) gave lower yields of VI and VII.

VI: yellow crystals. M.p. 151—152°C. Anal. Found: C, 44.05; H, 2.52. $C_{18}H_{12}O_6FeRu$ calcd.: C, 44.93; H, 2.51%. Mass spectrum (peaks corresponding to ^{56}Fe and ^{101}Ru): 481 (2; M^+), 453 (33), 425 (53), 397 (35), 369 (16), 341 (100), 313 (41) (successive loss of 6 CO), 101 (Ru^+), 56 (Fe^+). IR: ν(CO) 2064, 1987, 1972 ($Fe(CO)_3$), 2082, 2000, 1989 cm^{-1} ($Ru(CO)_3$). UV: 282(sh) (3195), 237 (7057).

VII: Yellow crystals. M.p. 132—133°C. Anal. Found: C, 45.09; H, 2.48. $C_{18}H_{12}O_6FeRu$ calcd.: C, 44.93; H, 2.51%. Mass spectrum: 481 (2; M^+), 453 (29), 425 (57), 397 (46), 369 (25), 341 (82), 313 (100) (successive loss of 6 CO), 101 (Ru^+), 56 (Fe^+). IR: ν(CO) 2089, 2062, 1998, 1988, 1986, 1974 cm^{-1}. UV: 330(sh) (7731), 255 (11410).

(b) (η^4-$C_{12}H_{12}$)$Fe(CO)_3$(*endo*) (IIIb) (0.28 g, 0.95 mmol) and $Ru_3(CO)_{12}$ (0.45 g, 0.7 mmol) were heated in toluene (75 ml) for 24 h. After filtration and removal of solvent, the residue was taken up in ether and chromatographed on Florisil using ether as eluent to remove unreacted $Ru_3(CO)_{12}$. Chromatography of the second fraction of yellow eluate on a 40 × 2 cm column packed with Florisil using n-hexane as eluent brought down a single yellow band which yielded complex VIII (0.21 g, 46%) after recrystallisation from n-pentane at —25°C.

VIII: Yellow crystals. M.p. 152—153°C. Anal. Found: C, 44.84; H, 2.42. $C_{18}H_{12}O_6FeRu$ calcd.: C, 44.93; H, 2.51%. Mass spectrum: 481 (90; M^+), 453 (<1), 425 (66), 397 (2), 369 (67), 341 (33), 313 (100) (successive loss of 6 CO), 154, 101 (Ru^+), 56 (Fe^+). IR: ν(CO) 2080, 2061, 1996, 1985, 1983, 1971 cm^{-1}. UV: 328(sh) (7210), 255 (11300).

(c) Complex IIa (0.2 g, 0.6 mmol) and $Fe_2(CO)_9$ (0.715 g, 2 mmol) were stirred in n-hexane (65 ml) at room temperature for 35 h. After filtration and removal of solvent, the residue was chromatographed on a 60 × 1 cm column packed with Florisil. Elution with n-hexane brought down a yellow band containing two complexes (0.081 g). After recrystallisation from n-pentane at —25°C, the two compounds were identified by M.p. and ^{1}H NMR as the di*exo* and *endo*, *exo* isomers of (η^4 : η^4-$C_{12}H_{12}$)$Fe_2(CO)_6$ (Vb, IVb).

(d) Complex IIa (0.15 g, 0.4 mmol) and (bza)$Fe(CO)_3$ [4] (0.18 g, 0.6 mmol) were heated in benzene (80 ml) at 60°C for 48 h. After filtration and removal of solvent, the residue was taken up in n-hexane/5 vol. % ether and chromatographed on a 40 × 2 cm column packed with Florisil using n-hexane as eluent. Three fractional recrystallisations from n-pentane gave IVa (9%), VII (16%) and VIII (9%).

IVa: Pale yellow crystals. M.p. 146—148°C. Anal. Found: C, 41.18; H, 2.32. $C_{18}H_{12}O_6Ru_2$ calcd.: C, 41.07; H, 2.30%. Mass spectrum: 526 (2; M^+), 498 (39), 470 (15), 442 (17), 414 (75), 386 (65), 358 (100) (successive loss of 6 CO), 101 (Ru^+). IR: ν(CO) 2079, 2001, 1989 cm^{-1}. UV: 266(sh) (5606), 239 (8240).

(e) $W(CO)_6$ (1.5 g, 4.3 mmol) was heated in dry and carefully degassed acetonitrile (120 ml) under reflux for two days. After removal of solvent, IIa (0.15 g, 0.44 mmol) and benzene (75 ml) were added and the mixture refluxed for 30 h. After filtration and removal of solvent, the residue was taken up in n-hexane/5 vol. % ether and chromatographed on a 60 × 2 column packed with Florisil. Elution with n-hexane/5 vol. % ether, then n-hexane/10 vol. % ether revealed a single orange band. After removal of solvent, the residue contained some unreacted $W(CO)_6$ which was eliminated by sublimation. Recrystallisation from n-pentane at 0° C yielded complex IXa (0.08 g, 30%).

IXa: Red crystals. M.p. 186° C (dec.). Anal. Found: C, 35.65; H, 2.06. $C_{18}H_{12}O_6RuW$ calcd.: C, 35.49; H, 1.99%. Mass spectrum (peaks corresponding to ^{101}Ru and ^{184}W): 609 (28; M^+), 581 (21), 553 (16), 525 (21), 497 (35), 469 (59), 441 (100) (successive loss of 6 CO), 220, 184 (W^+), 101 (Ru^+). IR: ν(CO) 2090, 2002, 1991 ($Ru(CO)_3$), 2000, 1942, 1908 cm^{-1} ($W(CO)_3$). UV: 392(sh) (893), 318 (15420), 268(sh) (11040), 217 (35000).

Oxidation of the bimetallic complexes

(a) Complex VI (0.05 g, 0.104 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (0.114 g, 0.208 mmol) were stirred in acetone (10 ml) at room temperature for 40 min (evolution of CO occurs upon mixing). Then water (30 ml) and ether (20 ml) were added, the ether extract washed with water (2 × 10 ml) and dried over $MgSO_4$. TLC and ^1H NMR showed the disappearance of VI and the presence of two complexes in approximately equal amounts (0.023 g). Chromatography on a 10 × 1 cm column packed with alumina grade II using ether as eluent gave after recrystallisation from n-pentane at —25° C complexes IIa and IIb (identified by its m.p., IR and ^1H NMR spectra [2]) in the molar ratio 0.54 ± 0.03/0.46 ± 0.03.

(b) Starting with complex VIII (0.05 g, 0.1 mmol) and workup as in (a) resulted in the complete disappearance of VIII after 35 min and the formation of IIIb as the sole product (0.027 g, 91%).

(c) Complex VII (0.04 g, 0.083 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (0.091 g, 0.166 mmol) were stirred in acetone (10 ml) at room temperature for 15 min. The reaction was quenched before completion (ca. 75%) and workup as in (a) gave a crystalline mixture (0.032 g) of IIIa and unreacted VII in the molar ratio 0.72 ± 0.04/0.28 ± 0.04 (measured by ^1H NMR). Using a ratio Ce^{IV}/VII = 2.8 provoked the complete disappearance of VII after 20 min and the formation of IIIa (94%).

(d) $(\eta^4:\eta^4\text{-}C_{12}H_{12})Fe_2(CO)_6$(*endo,exo*) (IVb) (0.25 g, 0.57 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (0.625 g, 1.14 mmol) were stirred in acetone (10 ml) at room temperature. The reaction was quenched after 15 min and workup as in (a) (using n-hexane instead of ether) gave a crystalline mixture (0.17 g) consisting of $(\eta^4\text{-}C_{12}H_{12})Fe(CO)_3$(*exo*) IIb, $(\eta^4\text{-}C_{12}H_{12})Fe(CO)_3$(*endo*) IIIb and unreacted diiron complex IVb in the molar ratio 0.05 ± 0.03/0.85 ± 0.03/0.10 ± 0.03. The same reaction using a molar ratio Ce^{IV}/IVb = 2.8 went to completion in 20 min and gave the same monoiron isomers IIb/IIIb (0.16 g, 98%) in the molar ratio 0.94 ± 0.03/0.06 ± 0.03.

(e) $(\eta^4:\eta^4\text{-}C_{12}H_{14})Fe_2(CO)_6$(*endo,exo*) (X) (0.1 g, 0.23 mmol) and $(NH_4)_2$-$[CeNO_3)_6]$ (0.25 g, 0.46 mmol) were stirred in acetonitrile (20 ml) at room temperature for 30 min. Acetonitrile was used since the reaction in acetone was too slow to go to completion before partial decomposition of the formed monometallic complexes and some polymerisation of the tetraene ligand prevented a clean workup. Separation of the unreacted diiron complex X and recrystallisation from n-pentane at —25° C gave a crystalline mixture of the *exo* and *endo* isomers $(\eta^4\text{-}C_{12}H_{14})Fe(CO)_3$ XI/XII in the molar ratio 0.59 ± 0.05/0.41 ± 0.05 (measured by ^1H NMR). The same reaction (0.34 mmol diiron complex) in acetone (20 ml, 30 min) using Me_3NO (0.05 g, 0.7 mmol) as oxidising agent gave the same *exo* and *endo* isomers and unreacted diiron complex X in the molar ratio 0.13 ± 0.04/0.15 ± 0.04/0.72 ± 0.04.

(f) Complex IXa (0.1 g; 0.164 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (0.182 g; 0.33 mmol) were stirred in acetone (10 ml) at room temperature for 5 min. Workup as in (a) gave IIa as the sole product (0.046 g; 0.135 mmol) after recrystallisation from n-pentane at −25°C. Yield 82%.

(g) IXb (0.2 g; 0.42 mmol) and $(NH_4)_2[Ce(NO_3)_6]$ (0.47 g; 0.86 mmol) were stirred in acetone (10 ml) at room temperature for 5 min. Then 10^{-3} *M* aqueous KOH (20 ml) and n-hexane (20 ml) were added, the organic extract washed with water (2 × 10 ml) and dried over $MgSO_4$. TLC and ^1H NMR showed the disappearance of IXb and the presence of a single product. Recrystallisation from n-pentane at −25°C gave IIb (0.092 g; 0.311 mmol). Yield 74%.

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