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Pericyclic organometallic reactions *. Cycloaddition reactions of (η^4-cycloheptatriene)Ru(CO)$_3$. Crystal structure of tricarbonyl[(2,3,4,9-η)-bicyclo[4.2.1]non-2-ene-4,9-diyl-7,7,8,8-tetracarbonitrile]ruthenium

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Abstract

(η^4-Cycloheptatriene)Ru(CO)$_3$ reacts readily with tetracyanoethylene (TCNE), 4-phenyltriazoline-3,5-dione (PTAD) and (carbomethoxy)maleic anhydride (CMA) to give stable 3+2 σ,π-allylic adducts. The 3+2 adduct with TCNE equilibrates via a [4,4]-sigmahaptotropic rearrangement with the less stable 6+2 adduct, which decomposes under the reaction conditions to the demetallated 6+2 adduct. It is concluded that σ,π-allylic adducts are in general more stable than their isomeric η^4-π counterparts. The structure of the 3+2 TCNE adduct was determined by a single-crystal X-ray diffraction study.

Introduction

η^4-Cycloheptatriene (cht) complexes of iron have become valuable probes for the study of pericyclic organometallic reactions. Typical examples involving the parent (cht)Fe(CO)$_3$ (I) are: the electrocyclic ring opening of (η^4-norcaradiene)Fe(CO)$_3$ (II) (eq. 1) [2], the 3 + 2 cycloaddition of I with tetracyanoethylene (TCNE) [3], and the subsequent [4,4]-sigmahaptotropic (σ,η) rearrangement [4] of the resulting adduct III to the formal 6 + 2 adduct IV (eq. 2). Similar cycloadditions of iron-coordinated tropone, heptafulvene, and azepine with a number of

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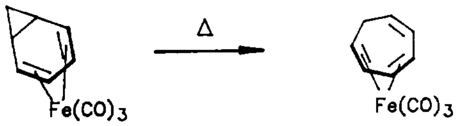
* For previous paper in this series see ref. 1.



I II

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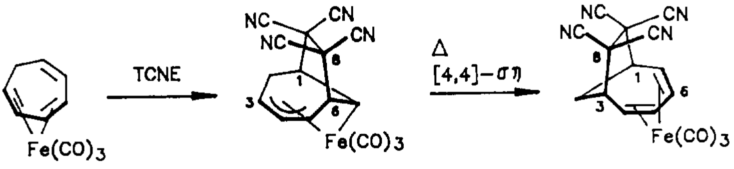

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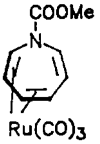

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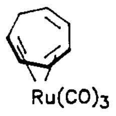


VI

electrophilic olefins have been observed, as have analogous (σ,η)-rearrangements of the corresponding adducts [5]. These studies all show that the course and kinetics of the reactions are both highly sensitive to the nature of the addends, the substituents on the organic ligand, and the ancillary metal ligands.

Few cycloaddition reactions of cht derivatives coordinated to transition metals other than iron have been described, although a report on cycloaddition reactions of (η^4-*N*-methoxycarbonylazepine)Ru$(CO)_3$ (V) with TCNE, hexafluoroacetone, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene appeared some time ago [6]. We considered it of interest to us to undertake a systematic study of the variations in reactivity caused by replacing the iron with other metals.

A natural choice was ruthenium, the next member of the iron triad. Since (cht)Ru$(CO)_3$ (VI) had recently become readily available [7], we focused our attention initially on this complex. We describe below the facile high-yield preparation and structural characterization of the novel adducts of (cht)Ru$(CO)_3$ (VI) with TCNE, 4-phenyltriazoline-3,5-dione (PTAD), and (carbomethoxy)maleic anhydride (CMA). We also compare the rearrangement aptitude of the Ru adducts under thermal conditions with that of their Fe counterparts.

Results

Cycloadditions

The reactions of (cht)Ru$(CO)_3$ VI with TCNE, PTAD and CMA were conducted in chloroform or acetone solutions; the reactions are fast and quantitative

Table 1

^{1}H NMR spectral data [a]

Complex	Solvent	H(1)	H(2s) [b]	H(2a)	H(3)	H(4)	H(5)	H(6)	H(7)
III [c]	$(CD_3)_2CO$	3.95	3.20	2.44	4.82	5.17	5.17	4.54	1.72
		J_{12s} 12.5, J_{12a} 2.8, J_{16} 1.2, J_{17} 6.3, J_{22} 18.0, J_{2s3} 6.3, J_{2a3} 1.8, J_{2a4} 1.0, J_{34} 9.0, J_{56} 7.0, J_{57} 1.0, J_{67} 9.8							
VII	$CDCl_3$	3.46	2.90	2.68	4.59	5.06	4.82	4.16	1.72
	$(CD_3)_2CO$	3.84	3.05	2.55	4.76	5.36	5.21	4.55	1.80
		[d] J_{12s} 12.0, J_{12a} 2.5, J_{16} 1.0, J_{17} 6.5, J_{22} 18.0, J_{2s3} 6.0, J_{2a3} 1.3, J_{2a4} 1.0, J_{34} 9.0, J_{35} 1.3, J_{45} 7.0, J_{46} 1.0, J_{56} 7.0, J_{57} 1.5, J_{67} 10.0							
VIII	$CDCl_3$	4.56	2.76	2.95	4.66	4.80	5.02	4.92	1.92
	$(CD_3)_2CO$	4.55	2.83	2.83	4.82	5.07	5.15	4.92	2.03
		aromatic: 7.3–7.55							
		[d] J_{12s} 8.5, J_{12a} 1.0, J_{13} 1.0, J_{17} 8.5, J_{22} 17.0, J_{2s3} 4.0, J_{2a3} 2.3, J_{2a4} 1.0, J_{34} 9.5, J_{35} 0.9, J_{45} 7.5, J_{46} 1.0, J_{56} 5.5, J_{57} 1.5, J_{67} 9.0							
IX	$CDCl_3$	3.20	2.87	2.53	4.53	4.56	4.74	3.95	1.32
		H(8) 3.65; Me(ester) 3.91							
		J_{12s} 11.5, J_{17} 7.2, J_{18} 1.0, J_{22} 16.5, J_{2s3} 4.5, J_{35} 1.5, J_{45} 6.3, J_{56} 6.2, J_{57} 1.5, J_{67} 9.0, J_{78} 1.0							

[a] δ (ppm) from TMS; J (Hz); [b] s = *syn*, a = *anti* to metal; [c] Ref. 4; [d] In $CDCl_3$.

at room temperature. The ^{1}H NMR spectrum of each reaction mixture showed the presence of a single product, which was isolated by crystallization from CH_2Cl_2–hexane.

The products were readily identified from their ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) as the 3 + 2 adducts VII, VIII, and IX, respectively (eq. 3). The

Table 2

^{13}C NMR spectral data [a]

Complex	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8,9)
III [b]	61.33	34.58	74.98	99.84	61.82	59.50	18.96	–
	CN: 112.17, 113.05; CO: 202.96, 210.90, 213.15							
VII [c]	62.1	34.8	69.7	105.8	59.7	61.1	13.7	51.8
	CN: 112.5, 113.4; CO: 189.2, 195.9, 198.1							
VIII [c]	62.99	41.87	72.13	103.52	64.11	61.76	18.31	–
	Ph: 125.39(*o*), 127.88(*p*), 129.02(*m*), 131.88(*i*) ring CO: 152.14, 153.41 ligand CO: 188.52, 195.06, 197.14							
J(CH) [d]	147	130	156	161	168	151	149	
IX [c]	52.73	41.22	71.98	103.13	60.72	60.72	14.78	59.50
	Me(ester): 53.53 ring CO: 165.06, 166.33, 171.73 ligand CO: 188.64, 195.98, 197.80							

[a] δ (ppm) from TMS; [b] In $(CD_3)_2CO$; [c] In $CDCl_3$; [d] Hz.

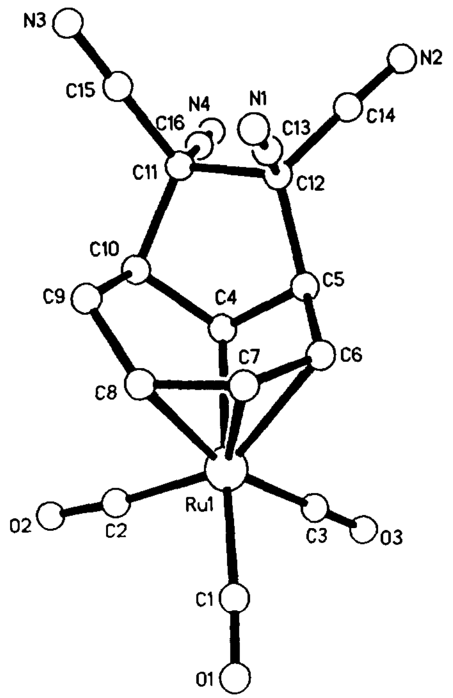
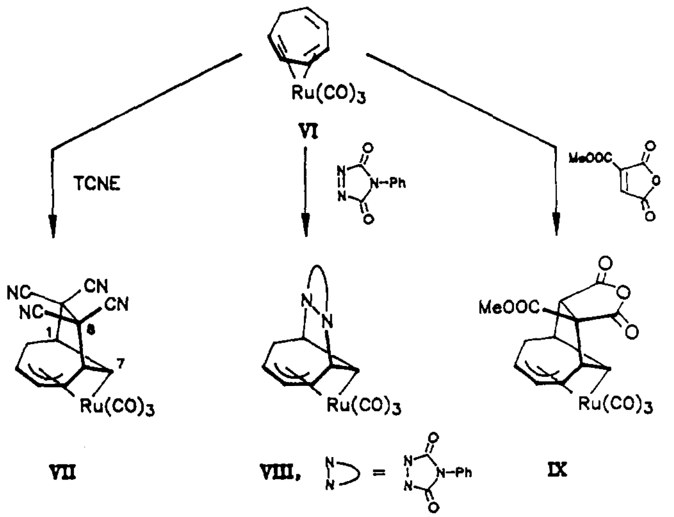


Fig. 1. Molecular structure of VII.

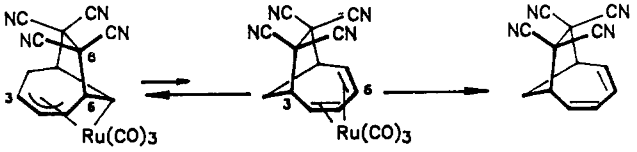
σ,π-allylic structure of the complexes was confirmed by comparison with the NMR spectra of III [4]. The structure of VII was confirmed by a single-crystal X-ray study (Fig. 1).



(3)

Thermal rearrangements

Heating of a degassed acetone solution of VII, under argon, in a sealed glass tube, at 55 °C for 24 h resulted in 83% recovery of the starting material and formation of 11% of the 6 + 2 diene complex X and 6% of the free diene XI [8] (by ^{1}H NMR). Prolonged heating under these conditions did not appreciably change the ratio between the complexes, but the amount of demetallated adduct XI increased. Similarly, when a chloroform solution of VII was kept for 6 months at room temperature, the ratio of VII:X:XI was 70:9:21. It should be noted that, unlike VII, the analogous σ,π-allylic iron compound III readily rearranges in acetone even at room temperature, solely to the 6 + 2 adduct IV [4] (eq. 4).



VII X XI

(4)

The PTAD 3 + 2 adduct VIII, like its TCNE counterpart, was stable and showed no tendency to undergo rearrangement in either chloroform or acetone. Interestingly, the analogous reaction of PTAD with (cht)Fe(CO)$_3$ (I) at room temperature did not give any isolable adduct, but the expected 3 + 2 adduct was identified by its ^{1}H NMR spectrum when the reaction was conducted at low temperatures [9].

Finally, the CMA adduct IX is also stable under rearrangement conditions at room temperature. However, prolonged heating at 55 °C in acetone resulted in extensive demetallation to give the uncoordinated formal 4 + 2 Diels–Alder adduct. No isomeric complex nor the free 6 + 2 adduct could be detected (by ^{1}H NMR). It is noteworthy that the corresponding 3 + 2 CMA adduct of I efficiently rearranges to the 4 + 2 complex at room temperature without decomposition [10].

Table 3

Bond lengths (Å) in compound VII

Ru(1)-C(1)	1.965(10)	Ru(1)-C(2)	1.902(11)
Ru(1)-C(3)	1.948(10)	Ru(1)-C(4)	2.149(9)
Ru(1)-C(6)	2.287(11)	Ru(1)-C(7)	2.225(10)
Ru(1)-C(8)	2.219(9)	C(1)-O(1)	1.121(12)
C(2)-O(2)	1.149(15)	C(3)-O(3)	1.127(13)
C(4)-C(5)	1.530(15)	C(4)-C(10)	1.522(11)
C(5)-C(6)	1.504(14)	C(5)-C(12)	1.607(11)
C(6)-C(7)	1.406(14)	C(7)-C(8)	1.422(16)
C(8)-C(9)	1.524(14)	C(9)-C(10)	1.528(13)
C(10)-C(11)	1.576(12)	C(11)-C(12)	1.589(14)
C(11)-C(15)	1.476(11)	C(11)-C(16)	1.472(14)
C(12)-C(13)	1.481(15)	C(12)-C(14)	1.472(13)
C(13)-N(1)	1.144(16)	C(14)-N(2)	1.141(13)
C(15)-N(3)	1.138(11)	C(16)-N(4)	1.138(16)

Table 4

Bond angles (°) in compound VII

C(1)-Ru(1)-C(2)	95.1(4)	C(1)-Ru(1)-C(3)	93.7(4)
C(2)-Ru(1)-C(3)	98.1(5)	C(1)-Ru(1)-C(4)	171.7(4)
C(2)-Ru(1)-C(4)	91.0(4)	C(3)-Ru(1)-C(4)	91.1(4)
C(1)-Ru(1)-C(6)	106.8(4)	C(2)-Ru(1)-C(6)	151.7(3)
C(3)-Ru(1)-C(6)	98.2(4)	C(4)-Ru(1)-C(6)	65.8(4)
C(1)-Ru(1)-C(7)	88.3(4)	C(2)-Ru(1)-C(7)	130.1(4)
C(3)-Ru(1)-C(7)	131.4(5)	C(4)-Ru(1)-C(7)	83.5(4)
C(6)-Ru(1)-C(7)	36.3(4)	C(1)-Ru(1)-C(8)	96.3(4)
C(2)-Ru(1)-C(8)	93.0(4)	C(3)-Ru(1)-C(8)	164.4(4)
C(4)-Ru(1)-C(8)	77.7(3)	C(6)-Ru(1)-C(8)	67.3(4)
C(7)-Ru(1)-C(8)	37.3(4)	Ru(1)-C(1)-O(1)	176.1(11)
Ru(1)-C(2)-O(2)	175.0(8)	Ru(1)-C(3)-O(3)	179.0(11)
Ru(1)-C(4)-C(5)	95.3(6)	Ru(1)-C(4)-C(10)	113.8(6)
C(5)-C(4)-C(10)	106.4(7)	C(4)-C(5)-C(6)	105.2(7)
C(4)-C(5)-C(12)	106.4(7)	C(6)-C(5)-C(12)	116.4(8)
Ru(1)-C(6)-C(5)	90.6(6)	Ru(1)-C(6)-C(7)	69.4(6)
C(5)-C(6)-C(7)	122.8(9)	Ru(1)-C(7)-C(6)	74.3(6)
Ru(1)-C(7)-C(8)	71.1(6)	C(6)-C(7)-C(8)	124.1(10)
Ru(1)-C(8)-C(7)	71.5(5)	Ru(1)-C(8)-C(9)	110.3(7)
C(7)-C(8)-C(9)	127.3(9)	C(8)-C(9)-C(10)	114.6(7)
C(4)-C(10)-C(9)	112.4(7)	C(4)-C(10)-C(11)	101.1(7)
C(9)-C(10)-C(11)	113.5(8)	C(10)-C(11)-C(12)	103.8(7)
C(10)-C(11)-C(15)	115.6(7)	C(12)-C(11)-C(15)	112.0(8)
C(10)-C(11)-C(16)	107.8(8)	C(12)-C(11)-C(16)	109.4(7)
C(15)-C(11)-C(16)	108.1(8)	C(5)-C(12)-C(11)	102.7(7)
C(5)-C(12)-C(13)	112.4(7)	C(11)-C(12)-C(13)	110.2(7)
C(5)-C(12)-C(14)	112.5(6)	C(11)-C(12)-C(14)	111.7(8)
C(13)-C(12)-C(14)	107.3(8)	C(12)-C(13)-N(1)	177.3(12)
C(12)-C(14)-N(2)	176.7(12)	C(11)-C(15)-N(3)	179.7(12)
C(11)-C(16)-N(4)	178.8(12)		

Solid-state structure of VII ($C_{16}H_8N_4O_3Ru$)

The crystal structure of VII confirmed the σ,π-allylic bonding mode of the Ru(CO)$_3$ fragment to the bicyclic ligand (Fig. 1). The Ru–C(allyl) bond distances all fall within the range 2.219–2.287 Å, whereas the Ru–C4 σ-bond is significantly shorter (2.149 Å) (Table 3). In the Ru(CO)$_3$ fragment, the Ru–C bond distances vary from 1.902 to 1.965 Å and the C–O distances from 1.121 to 1.149 Å. The Ru–C–O bond angles are all between 175.0 and 179.0° (Table 4).

The structure of VII is quite similar to that of its Fe analogue [11]. The M–C bond lengths in VII are slightly longer than in the Fe derivative, and this can be attributed mainly to the larger covalent radius of Ru. However, there is a more

Table 5

Selected metal–ligand bond lengths (Å) [a]

	M-C4	M-C6	M-C7	M-C8	M-C1	
VII	2.15	2.29	2.23	2.22	1.97	this work
III	2.09	2.17	2.08	2.11	1.82	Ref. 10

[a] Numbering as in Fig. 1.

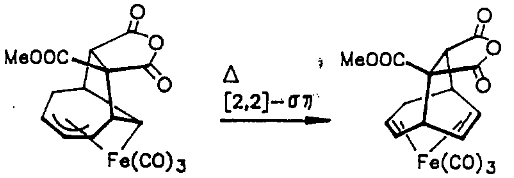
significant difference between the data for the M–C σ,π-allylic bonds. Although the Ru–C4(σ) bond in VII is shorter than any of the Ru–C(allyl) bonds, the Fe–C(σ) bond distance does not differ appreciably from the Fe–C(allyl) bond lengths (Table 5). This may indicate selective strengthening of the M–C σ-bond in the Ru derivative relative to its first row analogue. The opposite effect is observed, however, for the corresponding apical M–C(carbonyl) bonds.

Discussion

Two significant conclusions emerge from the above observations. First, the kinetically controlled cycloaddition reactions, like those involving the isolobal iron complexes, reveal a high periselectivity towards the $3+2$ σ,π-allylic adducts regardless of the choice of dienophile. It should be noted however, that whereas in the iron series some of the alternative $4+2$ adducts are also observed initially, none were detected here.

Second, the $3+2$ ruthenium adducts are much less prone to thermal sigmahaptotropic (σ,η) rearrangement than their iron counterparts. Thus, the Ru σ,π-allylic TCNE adduct VII only equilibrates via a [4,4]-σ, η shift with its butadiene isomer X, the former being more stable than the latter by ca. 1.5 kcal/mol. The reverse is true for the related iron analogues, for which the $3+2$ adduct III rearranges completely to the corresponding $6+2$ adduct IV, indicating that IV is more stable than III by at least 3.0 kcal/mol.

Likewise, the initial Ru $3+2$ adducts of PTAD (VII) resist thermal rearrangement, whereas their iron analogues are rather labile even at room temperature. Significantly, the initially formed $3+2$ Fe-CMA adduct XII rearranges entirely to the $4+2$ homobutadiene adduct XIII, via a [2,2]-σ,η shift [9] (eq. 5).



(5)

XII XIII

The variations in the structural and chemical properties of related transition metal complexes within the same triad have recently been examined by both experiment and theory. On the basis of the increase in the rotational barrier of η^2-complexes and charge localization in the fluxional $(C_7H_7)M(CO)_3^-$ anions of group 8 (M = Fe, Ru, Os) it was concluded that increase in metal–π^* backbonding interaction can be expected upon descending the triad [12].

Similarly, molecular orbital calculations of the strength of the $M–CH_3$ bond in $XM(CO)_n$ complexes were shown to increase down each of the two triads M = Mn, Tc, Re and M = Co, Rh, Ir, as a result of an increase in the σ-bonding overlaps [13].

A general increase in the energies of σ- and π-coordinated bonds upon descending the triad is therefore expected. Our observation that Ru σ,π-allylic complexes are more stable than the corresponding Fe counterparts also suggests that the contribution of σ-bonding to the complex stability predominates over the π-backbonding. This is further confirmed by early experiments relating to the stability of the metal–carbon σ bond in the (cyclooctadiene)M$(CO)_3$ series (M = Fe, Ru, Os) [14], and by the crystallographic data for VII and III (Table 5), which reveal a selective strengthening of the Ru–C relative to the Fe–C σ bond.

Experimental

General

IR spectra were recorded in KBr with a Nicolet 60 SXB FTIR. Mass spectra were determined by GLC-MS (Finnigan Model 4021 spectrometer). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM300 spectrometer. All reactions were conducted under argon.

TCNE (Aldrich) and PTAD [15] were sublimed. CMA was prepared by a modification of the procedure given by Hall et al. [16].

Tricarbonyl [(2,3,4,9-η)-bicyclo[4.2.1]non-2-ene-4,9-diyl-7,7,8,8-tetracarbonitrile] ruthenium (VII)

A solution of TCNE (94 mg, 0.73 mmol) in freshly distilled $CHCl_3$ (50 ml) was added with stirring to a $CHCl_3$ solution (10 ml) of tricarbonyl(η^4-cycloheptatriene)ruthenium (VI) (160 mg, 0.58 mmol). The reaction was instantaneous, as indicated by the absence of VI revealed by TLC analysis shortly after mixing of the reactants. The solvent was removed under reduced pressure and the solid residue crystallized from CH_2Cl_2–hexane to give colorless crystals of VII, m.p. 185–187 °C (dec.) (180 mg, 44% yield). IR (KBr): 2246 (CN), 2077, 2013 (CO) cm^{-1}; *m/e* (RA%) (DCI, NH_3): 407 (100, MH^+, based on the most abundant ^{102}Ru isotope), 186 (32). Anal. Found: C, 47.19; H, 1.99; N, 13.84. $C_{16}H_8N_4O_3Ru$ calcd.: C, 47.41; H, 1.99; N, 13.82%. ^1H NMR see Table 1; ^{13}C NMR see Table 2.

Tricarbonyl[(6,7,8,12-η)-2,3,5,6,9,10-hexahydro-1,3-dioxo-2-phenyl-5,10-methano-1H[1,2,4]-triazolo[1,2-a][1,2]diazocine-6,12-diyl]ruthenium (VIII)

A solution of sublimed PTAD (55 mg, 0.31 mmol) in freshly distilled $CHCl_3$ (5 ml) was added dropwise to a cooled (acetone–dry ice bath) and stirred $CHCl_3$ solution (5 ml) of VI (78 mg, 0.28 mmol) until the pale red colour of excess PTAD persisted. The mixture was left to warm up to room temperature, the solvent removed under reduced pressure, and the residue recrystallized from CH_2Cl_2–hexane to afford colourless crystals of VIII, m.p. 133–135 °C (dec.) (55 mg, 43% yield). IR (KBr): 2077, 1990 (ligand CO), 1759, 1710 (ring CO) cm^{-1}; *m/e* (RA%) (DCI, NH_3): 454 (12, MH^+), 241 (100), 195 (82). ^1H NMR see Table 1; ^{13}C NMR see Table 2. Anal. Found: C, 48.13; H, 3.16; N, 9.22. $C_{18}H_{13}N_3O_5Ru$ calcd.: C, 47.79; H, 2.90; N, 9.29%.

Tricarbonyl[(5,6,7,10-η)-methyl-1,3,3a,4,5,8,9,9a-octahydro-1,3-dioxo-4,9-methano-cycloocta[c]furane-5,10-diyl-3a-carboxylate]ruthenium (IX)

The solutions of VI (29 mg, 0.11 mmol) and CMA (20 mg, 0.13 mmol) in $CHCl_3$ (5 ml each) were mixed at room temperature. Removal of the solvent and crystallization from CH_2Cl_2–hexane afforded bright yellow crystals of IX, m.p. 159–161 °C (35 mg, 77% yield). IR (KBr) 2132, 2069, 1992 (ligand CO), 1844, 1773

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) of compound VII

	x	y	z	U_{eq} [a]
Ru(1)	5056(1)	1607(1)	2832(1)	323(2)
C(1)	5071(16)	−401(11)	3427(8)	407(34)
O(1)	4995(13)	−1542(8)	3796(7)	545(31)
C(2)	3303(15)	1978(10)	3722(8)	382(31)
O(2)	2318(11)	2314(9)	4266(7)	517(29)
C(3)	3267(17)	684(11)	1503(9)	465(37)
O(3)	2237(15)	131(11)	737(8)	770(39)
C(4)	5476(15)	3867(9)	2203(7)	334(29)
C(5)	7049(13)	3756(9)	1551(7)	313(28)
C(6)	7706(14)	2425(10)	2008(8)	363(31)
C(7)	8198(15)	2290(11)	3156(9)	400(32)
C(8)	7534(15)	3007(10)	4005(8)	380(31)
C(9)	7478(15)	4680(10)	4100(7)	365(31)
C(10)	6357(14)	5178(9)	3093(7)	318(28)
C(11)	7621(14)	6411(9)	2413(7)	325(28)
C(12)	8584(13)	5423(9)	1716(7)	313(28)
C(13)	10415(16)	5373(11)	2350(8)	404(34)
N(1)	11809(15)	5357(11)	2877(8)	534(37)
C(14)	8967(15)	6095(10)	649(8)	387(33)
N(2)	9173(16)	6599(11)	−194(8)	563(39)
C(15)	9031(15)	7709(10)	3085(8)	392(32)
N(3)	10115(15)	8707(10)	3607(8)	533(35)
C(16)	6357(16)	7053(10)	1644(8)	402(34)
N(4)	5360(16)	7549(11)	1064(8)	544(38)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

(anhydride CO), 1724 (ester CO); m/e (RA%) (CI, NH_3): 435 (14, MH^+), 266 (100). ^1H NMR see Table 1; ^{13}C NMR see Table 2. Anal. Found: C, 44.08; H 2.83. $C_{16}H_{12}O_8Ru$ calcd.: C, 44.35; H, 2.79%.

Thermal rearrangements

The thermolysis of the 3 + 2 adducts was conducted in degassed (three freeze–thaw cycles) acetone solutions (ca. 20%) which were sealed under argon and placed in a constant temperature oil bath. Sample tubes were cooled and opened, and the mixture filtered through Celite. The solvent was removed under reduced pressure, the residue was dissolved in $CDCl_3$, and the product ratio determined by integration from the ^1H NMR spectrum of the mixture.

Crystallographic experimental details

A crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was sealed in a thin-walled glass capillary tube and mounted on a Siemens R3m/V diffractometer. The crystal system (triclinic) was revealed after centring of 18 strong reflections with 2θ values between 22.0 and 38.0 °. Data were collected at $-70\,°C$ over a 2θ range of 4.0 to 55.0 ° using the Wyckoff scan technique. The structure was solved by direct methods in space group $P\bar{1}$ and subsequently refined to convergence after a series of full-matrix least-squares calculations (Siemens SHELXTL PLUS software) [17]. All non-hydrogen atoms were refined anisotropically (Table 6); hydrogen atoms were positionally refined with a common refined isotropic temperature factor. Final

Table 7

Crystal structure and refinement data for compound VII

Empirical formula	$C_{16}H_8N_4O_3Ru$
Formula weight	405.3
Crystal size, mm	0.2×0.2×0.3
Space group	$P\bar{1}$
Cell constants	
a, Å	7.454(4)
b, Å	9.025(2)
c, Å	12.139(3)
α, deg	91.10(2)
β, deg	98.18(3)
γ, deg	106.07(3)
Cell vol., Å^3	775.3(5)
Z	2
D_{calc}, g/cm^3	1.736
μ_{calc}, cm^{-1}	10.12
Diffractometer used	Siemens R3m/V
Scan type	Wyckoff
Radiation	Mo-K_α(λ = 0.71073 Å)
Monochromator	highly-oriented graphite crystal
Scan width, deg	1.40
No. of standard reflections	3 per 97 reflections
2θ range, deg	4.0 to 55.0
Range of h, k, l	$+9$, ± 11, ± 15
No. of unique reflections	3579
No. of observed reflections	3438 ($F > 6.0\ \sigma(F)$)
No. of parameters refined	242
Weighting scheme	unit weights
Quantity minimized	$\Sigma w(F_{obs} - F_{calc})^2$
$R = \Sigma \lvert F_{obs} - F_{calc} \rvert / \Sigma \lvert F_{obs} \rvert$	8.63%
$Rw = [\Sigma w(F_{obs} - F_{calc})^2 / \Sigma w(F_{obs})^2]^{1/2}$	10.13%

R-values for 3438 reflections having I greater than $3\sigma(I)$ were $R = 8.63\%$ and $wR = 10.13\%$ (Table 7). Tables of thermal parameters, hydrogen atom coordinates, and structure factors are available from the authors.

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