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Butadienic Derivatives of Metal Carbonyls
II. Some Rearrangements of butadienic Ligands in Reactions with Dodecacarbonyltriruthenium[1]

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Isomerization and rearrangement of ligands L, such as 1,4-trans,trans-diphenyl-1,3-butadiene, hexadiene isomers, isoprene and 1,3-butadiene, occur in the reactions with $Ru_3(CO)_{12}$ to give trimetallic complexes of molecular formula $HRu_3(CO)_9(L–H)$, in addition to bi- and monometallic complexes of known structure. On the contrary the diene skeleton is always maintained when L is 2,3-dimethyl-1,3-butadiene. Structures of $HRu_3(CO)_9(L–H)$ complexes are suggested and some novel features in their proton n.m.r. spectra are described.

Introduction

Dodecacarbonyltriruthenium and -triosmium have been shown to react with alkynes and give a good yield of complexes containing a heterocyclic five-membered ring with σ metal–carbon bonds.[2–8] Two alkyne molecules have been shown to join and form the metal-cyclopentadiene systems. In order to test formation of the same compounds from butadienic skeleton ligands we have reacted dodecacarbonyltriruthenium with 1,2,3,4-tetraphenyl-1,3-butadiene and 1,4-*trans,trans*-diphenyl-1,3-butadiene.[1] The characterisation of compounds has provided evidence that only the orange isomer $Ru_3(CO)_8L_2$, where L = C_2Ph_2 or C_2HPh, can be prepared from both arylacetylene and arylbutadiene ligands. We have extended this study and herein report the detailed results about reactions of dodecacarbonyltriruthenium and a number of aryl- and alkylbutadiene ligands.

Experimental

All solvents were dried on molecular sieves.

I.r. spectra were recorded on a Beckman Model IR 12 double-beam spectrophotometer with KBr optics. ^{1}H n.m.r. spectra of (I) were obtained with a Varian 100 XL spectrometer, while the ^{1}H n.m.r. spectra of the other complexes with a Jeol 60 HL spectrometer. The mass spectra were recorded on a Perkin–Elmer Hitachi RMU6H mass spectrometer using an ionizing energy of 70 ev.

Reaction of 1,4-trans,trans-diphenyl-1,3-butadiene with $Ru_3(CO)_{12}$

0.400 g (0.63 mmol) of $Ru_3(CO)_{12}$ were reacted with 0.130 g (0.63 mmol) of 1,4-*trans,trans*-diphenyl-1,3-butadiene in 700 ml of benzene under reflux for 24 hours. The cooled solution was filtered, concentrated and separated by TLC (using light petroleum and diethyl ether, 19:1 v/v, as eluent on kieselgel $PF_{254+366}$) to give four compounds (I), (II), (III) and (IV), recrystallized from n-heptane at 0° C. Anal. Calcd. for $C_{25}H_{14}O_9Ru_3$: C, 39.42; H, 1.85; O, 18.71; Ru, 39.62. Found for (1): C, 39.11; H, 2.4; O, 18.17; Ru, 40.1%. Calcd. for $C_{22}H_{12}O_6Ru_2$: C, 45.99; H, 2.11; O, 16.71; Ru, 35.19. Found for (II): C, 45.48; H, 2.6; O, 16.93; Ru, 34.3%. Calcd. for $C_{19}H_{14}O_3Ru$: C, 58.30; H, 3.60; O, 12.26; Ru, 25.83. Found for (III): C, 57.90; H, 3.8; O, 12.30; Ru, 24.9%. Mass spectrum of (I): m/e 764 $[M]^+$ followed by loss of nine carbonyl groups; mass spectrum of (II): m/e 576 $[M]^+$ followed by loss of six carbonyl groups; mass spectrum of (III): m/e 392 $[M]^+$ followed by loss of three carbonyl groups; mass spectrum of (IV): m/e 734 $[M]^+$ followed by loss of eight carbonyl groups.

Reactions of 2,4-trans,trans-hexadiene with $Ru_3(CO)_{12}$

Dodecacarbonyltriruthenium (0.300 g, 0.47 mmol) and 2,4-*trans,trans*-hexadiene (1.0 ml, 8.6 mmol) dissolved in benzene (700 ml) were refluxed for 7 hours. The solution was filtered and concentrated under reduced pressure and separated by TLC (absorbent and eluent as above) to give three yellow compounds (V), (VI) and (VII). The same compounds were obtained in similar yields when 2,4-*cis,trans*-hexadiene or 1,5-hexadiene were used as ligands. Anal. Calcd. for $C_{15}H_{10}O_9Ru_3$: C, 28.26; H, 1.58; O, 22.59; Ru, 47.57.

Found for (V): C, 29.12; H, 1.9; O, 22.80; Ru, 46.5%. Calcd. for $C_9H_{10}O_3Ru$: C, 40.44; H, 3.77; O, 17.96; Ru, 37.82. Found for (VII): C, 39.90; H, 4.5; O, 17.80; Ru, 38.5%. Mass spectrum of (V): m/e 640 $[M]^+$ followed by loss of nine carbonyl groups; mass spectrum of (VII): m/e 268 $[M]^+$ followed by loss of three carbonyl groups.

Isomerization of (V) to (VI)

0.030 g of (V) were heated in n-heptane under reflux. The isomerization, followed by i.r. spectroscopy in ν (CO) region, was complete after two hours.

Reaction of isoprene with $Ru_3(CO)_{12}$

0.300 g (0.47 mmol) of $Ru_3(CO)_{12}$ and 1.0 ml (10 mmol) of isoprene dissolved in benzene (700 ml) were refluxed for 11 hours. The solution was filtered, concentrated under reduced pressure and separated by TLC (absorbent and eluent as above) to give as main products yellow crystals of (VIII) and (IX). Anal. Calcd. for $C_{14}H_8O_9Ru_3$: C, 26.97; H, 1.29; O, 23.09; Ru, 48.64. Found for (VIII): C, 27.70; H, 2.2; O, 23.90; Ru, 48.4%. Calcd. for $C_{11}H_6O_6Ru_2$: C, 30.28; H, 1.36; O, 22.00; Ru, 46.37. Found for (IX): C, 30.51; H, 1.8; O, 21.75; Ru, 45.8%. Mass spectrum of (VIII): m/e 626 $[M]^+$ followed by loss of nine carbonyl groups; mass spectrum of (IX): m/e 438 $[M]^+$ followed by loss of six carbonyl groups.

Reaction of 2,3-dimethyl-1,3-butadiene with $Ru_3(CO)_{12}$

A solution of dodecacarbonyltriruthenium (0.300 g, 0.46 mmol) and 2,3-dimethyl-1,3-butadiene (1.0 ml, 9.1 mmol) in benzene (700 ml) was heated under reflux for 8 hours. The cooled solution was filtered and concentrated under reduced pressure and separated by TLC as above. A first band contained a yellow compound (X) as main product and a little yield of a complex obtained by further purification and characterised as $Ru_3(CO)_8C_6H_8$ isomer with bridging carbonyl groups (XI), while a second band gave (XII). Anal. Calcd. for $C_{12}H_8O_6Ru_2$: C, 32.00; H, 1.79; O, 21.31; Ru, 44.89. Found for (X): C, 32.51, H, 1.9; O, 20.95; Ru, 44.6%. Calcd. for $C_9H_{10}O_3Ru$: C, 40.44; H, 3.77; O, 17.96; Ru, 37.83. Found for (XII): C, 40.25; H, 4.0; O, 17.80; Ru, 37.7%. Mass spectrum of (X): m/e 452 $[M]^+$ followed by loss of six carbonyl groups; mass spectrum of (XI): m/e 610 $[M]^+$ followed by loss of eight carbonyl groups; mass spectrum of (XII): m/e 268 $[M]^+$ followed by loss of three carbonyl groups.

Reaction of 1,3-butadiene with $Ru_3(CO)_{12}$

A slow stream of 1,3-butadiene was bubbled into a solution of $Ru_3(CO)_{12}$ (0.300 g) in refluxing benzene (700 ml) for 6 hours. The solution was filtered and concentrated. Separation by TLC, as above, gave one compound in good yield as yellow crystals (XIII). Anal. Calcd. for $C_{13}H_6O_9Ru_3$: C, 25.62; H, 0.99; O, 23.63; Ru, 49.76. Found for (XIII): C, 24.96; H, 1.7; O, 23.78; Ru, 50.1%. Mass spectrum of (XIII): m/e 612 $[M]^+$ followed by loss of nine carbonyl groups.

Results and Discussion

When dodecacarbonyltriruthenium is heated under reflux in benzene with 1,4-*trans,trans*-diphenyl-1,3-butadiene three yellow complexes of molecular formula $Ru_3(CO)_9C_4H_4Ph_2$ (I), $Ru_2(CO)_6C_4H_2Ph_2$ (II) and $Ru(CO)_3C_4H_4Ph_2$ (III) are obtained, in addition to the orange isomer $Ru_3(CO)_8C_4H_2Ph_2$ (IV) analogous to $Ru_3(CO)_8C_4Ph_4$.[5]

The proton n.m.r. spectrum of (I) shows a doublet at τ 31.0 indicating the presence of a hydrido ligand, which was shown to be longe-range coupled, by double resonance experiments, with the doublet centered at τ 2.88 (J = 2.5 Hz), assigned to the H–C(2) proton. (Figures 1a and 1b.) The quadruplet at τ 5.90 assigned to the methylene protons is consistent with an AB system and coalesces to a singlet at about 60° C. Upon cooling the CH_2 resonance appears again as the previous quadruplet. A complex multiplet at τ 2.65 is due to ten aromatic protons. The n.m.r. spectrum of (I) at 23° C is shown in Figure 1a and the effect of temperature on the quadruplet in Figure 2. These data together with i.r. (Table I) and mass spectra suggest for (I), reformulated as $HRu_3(CO)_9C_4H_3Ph_2$, the structure of Figure 3, in which the hydrido ligand is not shown. (I) is assumed to be analogous to $HRu_3(CO)_9C_6H_9$.[9] Complex (II) exhibits features characteristic of corresponding compounds prepared from dodecacarbonyltriiron and -triruthenium with substituted acetylenes, while (III) is considered to be similar to $Fe(CO)_3C_4H_6$.[10]

The reactions of $Ru_3(CO)_{12}$ with *trans,trans* and *cis,trans*-isomers of 2,4-hexadiene and with 1,5-hexadiene afford the same three main products in similar yields. This fact implies isomerization of the organic molecules during the formation of these complexes and confirms that the presence of butadiene skeleton is not an essential prerequisite.[11] Two complexes are isomers of molecular formula $Ru_3(CO)_9C_6H_{10}$ (V) and (VI) and the third is $Ru(CO)_3C_6H_{10}$ (VII). Complex (VI) has been reported previously[1,9] and its structure, containing a pseudo π-allyl moiety, well established. Mass and i.r. spectra of (V) are very similar to those of (VI), but its proton n.m.r. spectrum is completely different. (V) does, in fact, exhibit a singlet at τ 30.6 (1 H), a quartet at τ 6.48 (1 H), a doublet at τ 8.35 (3 H) and two signals at τ 8.86 and 7.14 due to methyl and methylene protons coupled together. Thus one can argue that the ligand acts as a five elec-

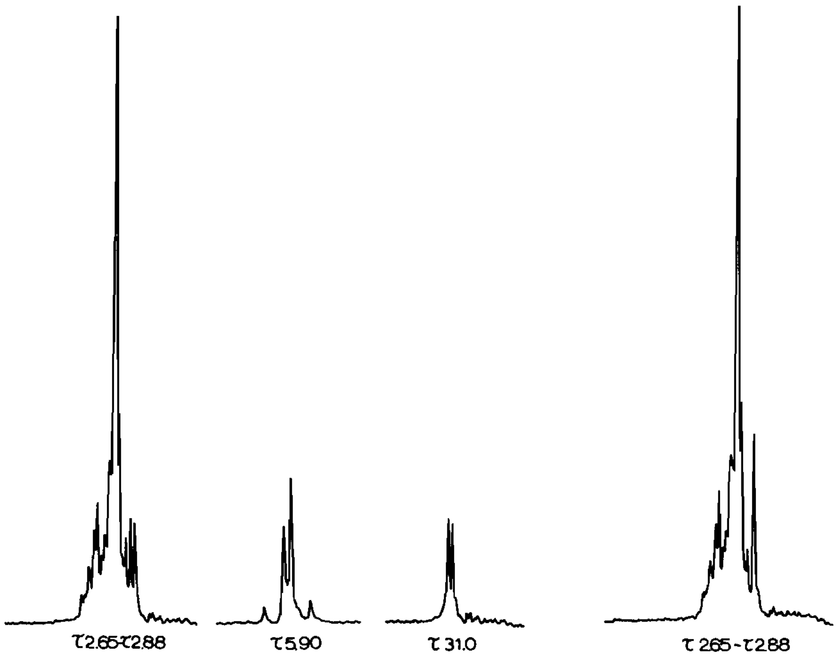

Figure 1a. Proton n.m.r. spectrum of $HRu_3(CO)_9C_4H_3Ph_2$ (I); (b) the same in the range τ 2.5–3.5, irradiated at τ 31.0.

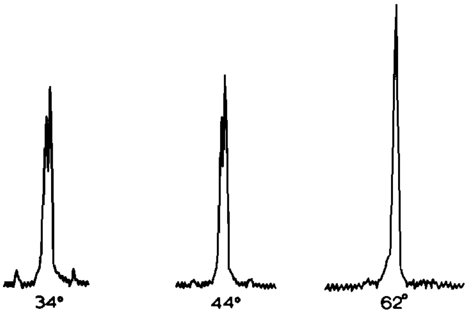

Figure 2. Proton n.m.r. spectrum of methylene protons of (I) as function of temperature.

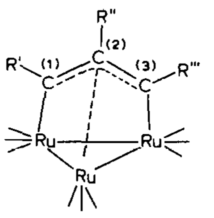

Figure 3. Structure of pseudo π-allyl complexes (I), (VI), (VIII) and (XIII).

(I)	R' = Ph	R'' = H	R''' = CH_2Ph
(VI)	R' = CH_3	R'' = H	R''' = CH_2CH_3
(VIII)	R' = H	R'' = CH_3	R''' = CH_3
(XIII)	R' = H	R'' = H	R''' = CH_3

TABLE I. Carbonyl stretching frequencies[a].

	Complex	ν (CO), cm^{-1}
(I)	$HRu_3(CO)_9C_4H_3Ph_2$	2097ms, 2072s, 2044vs, 2030s, 2016s, 2004ms, 1999m, 1983shw, 1962w
(II)	$Ru_2(CO)_6C_4H_2Ph_2$	2080s, 2049vs, 2013vs, 1998shs, 1957w
(III)	$Ru(CO)_3C_4H_4Ph_2$	2063s, 2001vs, 1996vs
(IV)	$Ru_3(CO)_8C_4H_2Ph_2$	2072m, 2033vs, 2014s, 1984s, 1884m, 1860m
(V)	$HRu_3(CO)_9C_6H_9$	2094ms, 2066s, 2042vs, 2025s, 2020shm, 2005ms, 1998m, 1984w
(VII)	$Ru(CO)_3C_6H_{10}$	2056s, 1992vs, 1983s
(VIII)	$HRu_3(CO)_9C_5H_7$	2097ms, 2069s, 2043vs, 2026s, 2015s, 2004s, 1996m, 1963w
(IX)	$Ru_2(CO)_6C_5H_6$	2083ms, 2053vs, 2012s, 1998ms, 1986ms
(X)	$Ru_2(CO)_6C_6H_8$	2081ms, 2050vs, 2009s, 1995ms, 1984ms
(XI)	$Ru_3(CO)_8C_6H_8$	2071m, 2027vs, 2008s, 1980s, 1889m, 1866m
(XII)	$Ru(CO)_3C_6H_{10}$	2064s, 1997vs, 1987vs
(XIII)	$HRu_3(CO)_9C_4H_5$	2098ms, 2071s, 2046vs, 2028s, 2017ms, 2009s, 1999m, 1984shw, 1966 w

[a] Carbon tetrachloride solution, except for (I), (VIII) and (XIII) (n-heptane).

tron donor and contains a central C_3 unit associated with the metal cluster. At least one carbon atom being reasonably linked to a ruthenium atom by a σ bond, a suggested bonding scheme, shown in Figure 4a, consists of a σ bond from C(1) to one ruthenium atom and four π-type electrons donated to the cluster from C(2)C(3) moiety. As alternative hypothesis (Figure 4b) we assume three σ metal–carbon bonds and donation to the cluster of two π-type electrons from C(2)C(3) moiety. The hydrido ligand, whose position cannot be located, must give one electron to the cluster to satisfy the effective atomic number rule. It is not shown in Figures 4a and 4b, but is likely to bridge two metal atoms or the whole cluster. The yield of (V) increases when the reaction temperature is lower than usual and this fact was explained when (V) was completely converted to (VI) after heating under reflux in n-heptane for about two hours. Evidence is so obtained that (V) is the initial product in the reaction of $Ru_3(CO)_{12}$ and hexadienes. Apart from the loss of three carbonyl groups it seems likely that the attack of the ligand causes rearrangement of two hydrogen atoms: one shifts to the cluster and forms metal–hydrogen bonds and the other to a carbon atom in α position with respect to the C_3 unit. Preliminary results indicate that complexes with the same structure can also be observed as products of the reaction of the reaction of $Ru_3(CO)_{12}$ with some alkylacetylene ligands. A further rearrangement of the organic moiety occurs in the reaction which gives (VI) from (V). It mainly consists of hydrogen migration from C(1) to C(2) with consequent formation of the pseudo π-allyl unit (Figure 3).

Reactions of dodecacarbonyltriruthenium and isoprene yield two main products, whose molecular formulas are $Ru_3(CO)_9C_5H_8$ (VIII) and $Ru_2(CO)_6C_5H_6$ (IX). The proton n.m.r. spectrum of (VIII) exhibits a highfield singlet at τ 31.3, two singlets at τ 7.22 and 7.72 assigned to methyl protons bonded to C(2) and C(3) and an anomalous downfield singlet at τ 1.45 assignable to H–C(1) proton. These data and i.r. absorption bands show (VIII) is $HRu_3(CO)_9C_5H_7$, isostructural with (I) and (VI) (Figure 3). I.r. and mass spectra of (IX) might suggest the usual structure containing a tricarbonylruthenium moiety π bonded to a rutheniacyclopentadiene five-membered ring, but complexity of its n.m.r. spectrum seems not to confirm this hypothesis.

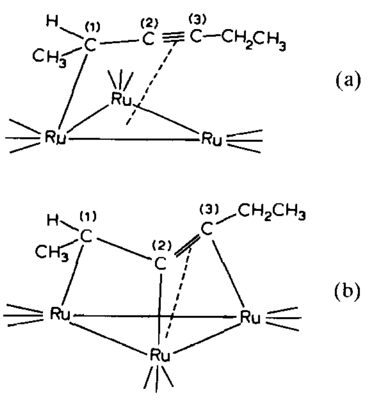

Figure 4. Suggested structures of $HRu_3(CO)_9C_6H_9$(V).

Treatment of dodecacarbonyltriruthenium with 2,3-dimethyl-1,3-butadiene gives $Ru_2(CO)_6C_6H_8$ (X) and $Ru(CO)_3C_6H_{10}$ (XII) in good yield, which one can assigne to the usual structures above considered for bi- and monometallic complexes. (X) exhibits n.m.r. signals (Table II) assignable to olefinic protons at very low values with respect to those usually encountered for olefinic protons π bonded to metal atoms. $Ru_3(CO)_8C_6H_8$ isomer with bridging carbonyl groups (XI)[6] was observed in low yield, but it could not be completely separated from (X). However its presence demonstrates the usual sequence from tri- to bi-metal-

TABLE II. Proton n.m.r. spectra[a].

	Complex	Chemical shift τ	Relative Intensity
(I)	$HRu_3(CO)_9C_4H_3Ph_2$	2.65m	10
		2.88d	1
		5.90q	2
		31.0d	1
(II)	$Ru_2(CO)_6C_4H_2Ph_2$	2.85m	10
		3.51s	2
(III)	$Ru(CO)_3C_4H_4Ph_2$	2.95m	10
		4.20q	2
		7.45q	2
(V)	$HRu_3(CO)_9C_6H_9$	6.48q	1
		7.14q	2
		8.35d	3
		8.86t	3
		30.6s	1
(VIII)	$HRu_3(CO)_9C_5H_7$	1.45s	1
		7.22s	3
		7.72s	3
		31.3s	1
(IX)	$Ru_2(CO)_6C_5H_6$	2.85d	1
		3.4–3.8m	2
		7.68s	3
(X)	$Ru_2(CO)_6C_6H_8$	3.26s	2
		7.70s	6
(XII)	$Ru(CO)_3C_6H_{10}$	7.80s	3
		8.31d	1
		9.72d	1
(XIII)	$HRu_3(CO)_9C_4H_5$	1.38d	1
		3.02dd	1
		7.15s	3
		31.3d	1

[a] Carbon tetrachloride solution.

lic complexes well known for compounds prepared from acetylenic ligands.

When 1,3-butadiene is used as ligand in benzene under reflux, several complexes are obtained. The major product was initially characterised as $Ru_3(CO)_9C_4H_6$ (XIII) by its mass spectrum, whilst the very little yields prevented the identification of the other compounds. The proton n.m.r. spectrum indicates (XIII) is analogous to (I), (VI) and (VIII), because it exhibits a highfield absorption coupled with the proton bonded to the central atom of the pseudo π-allyl system. The anomalous downfield doublet at τ 1.38, already observed in the spectrum of (VIII), is assigned to the H–C(1) proton and appears to be coupled with the H–C(2) proton.

The proton n.m.r. spectra of the trimetallic complexes described herein permit us to make some general remarks. In the case of (I), (VI), (XIII) the longe-range coupling between H–C(2) and the metal-bonded proton is similar to that reported by Bruce and coworkers for $HRu_3(CO)_9C_{12}H_{15}$.[11] On the other hand the H–C(1) proton of (V), (VIII) and (XIII) appears as a singlet, but a very small coupling constant with the metal-bonded hydrogen cannot be excluded. Moreover the H–C(1) proton of (VIII) and (XIII) displays an anomalous downfield shift (Table II), rather unusual for either organometallic or unsatured organic compounds, analogous to figures reported for complexes containing ligands σ–π bonded to metal atoms.[12] The mass spectra of these two compounds show particular fragmentation patterns after the loss of all carbonyl groups. Envelopes due to superimposed bimetallic ions are, in fact, present in good intensity corresponding to Ru_2L^+, $Ru_2(L{-}H)^+$, $Ru_2(L{-}2H)^+$ and $Ru_2C_3^+$. The other triruthenium complexes display bimetallic ions in very low abundance. It is noteworthy that this deshielding effect is also experienced by protons bonded to carbon atoms adjacent to the C_3 unit, as is the situation for the methylene protons of (I), methylene and methyl protons of (VI) and methyl protons of (VIII) and (XIII). These data can tentatively be ascribed to a partial carbenoid character of C(1) and C(3). Investigation are however in progress to clarify the relative importance of factors affecting these novel behaviours and possibly also the non-equivalence of methylene protons in (I) and (VI).

With respect to used ligands dodecacarbonyltriruthenium shows a reactivity similar to that reported with 1,5,9-cyclododecatriene[11], the main difference being the preferential loss of two hydrogen atoms in the reaction with the cyclic ligand. In addition to isomerization of double bonds $Ru_3(CO)_{12}$ brings about hydrogen rearrangement processes in the molecule of ligands during formation of the complexes. It is likely that the presence of at least one hydrogen atom in α position to a double bond is essential for the rearrangement to occur, because 2,3-dimethyl-1,3-butadiene does not afford structures reported in Figures 3 and 4, but complexes where the diene skeleton is maintained.

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