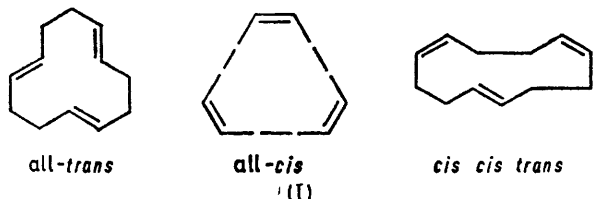


## Reactions Between Cyclododeca-1,5,9-triene and Dodecacarbonyltriruthenium

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Interaction of cyclododeca-1,5,9-triene (CDT) isomers with  $\text{Ru}_3(\text{CO})_{12}$  gives four complexes, characterised as  $\text{HRu}_3(\text{CO})_9(\text{C}_{12}\text{H}_{15})$ ,  $\text{HRu}_3(\text{CO})_9(\text{C}_{12}\text{H}_{17})$ ,  $\text{HRu}_3(\text{CO})_7(\text{C}_{12}\text{H}_n)_2$  ( $n$  probably 17), and  $\text{Ru}_4(\text{CO})_{10}(\text{C}_{12}\text{H}_{16})$ . Spectroscopic properties of the complexes are described, as are some reactions with phosphorus donor ligands. The results are discussed in terms of the structures of the complexes, two of which had been determined previously by X-ray methods.

SINCE the discovery of the formation of cyclododeca-1,5,9-triene [CDT (I)] by the trimerisation of buta-1,3-diene on Ziegler-type catalysts,<sup>1</sup> complexes of this large cyclic unsaturated hydrocarbon have been described for titanium,<sup>2</sup> rhodium,<sup>3</sup> nickel,<sup>4</sup> palladium,<sup>5,6</sup> platinum,<sup>5,7</sup> copper,<sup>5,8</sup> silver,<sup>1,5,9</sup> and gold.<sup>10</sup> In addition, the isomerisation to *trans*-bicyclo[6,4,0]dodecadiene by iron carbonyl, with isolation of the corresponding diene-Fe(CO)<sub>3</sub> complex, has been mentioned briefly.<sup>11</sup> Herein we report the initial results of a study of the reactions of CDT with  $\text{Ru}_3(\text{CO})_{12}$ .



Dodecacarbonyltriruthenium reacts slowly with all-*trans*-, all-*cis*-, and *cis,cis,trans*-isomers of CDT in re-

fluxing light petroleum to give four complexes initially characterised as  $\text{C}_{12}\text{H}_{16}\text{Ru}_3(\text{CO})_9$  (II),  $\text{C}_{12}\text{H}_{18}\text{Ru}_3(\text{CO})_9$  (III),  $\text{C}_{24}\text{H}_{34}\text{Ru}_3(\text{CO})_7$  (IV), and  $\text{C}_{12}\text{H}_{16}\text{Ru}_4(\text{CO})_{10}$  (V), which could be separated by chromatography of the reaction mixture on Florisil. Complex (II) was obtained in high yield (*ca.* 70%), and was accompanied by smaller amounts of the other three complexes. In all cases, the gross empirical formula could be determined by conventional analyses (Table 1), but uncertainty remained in the number of hydrogen atoms. This problem was partially resolved by the use of high-resolution mass spectrometry. The  $\nu(\text{CO})$  regions of their infrared spectra (Table 2) were complex, and contributed little to the determination of the structures. The proton n.m.r. spectra (Table 3) were also complex; those of complexes (II), (III), and (IV) exhibited high-field signals, indicating the presence of metal-bonded protons.

At this stage, recourse was made to single-crystal X-ray analyses, although satisfactory crystals could only be obtained for complexes (II) and (V). Full accounts

<sup>1</sup> H. Breil, P. Heimbach, M. Kröner, H. Müller, and G. Wilke, *Makromol. Chem.*, 1963, **69**, 18.

<sup>2</sup> H. Weber, W. Ring, U. Hochmuth, and W. Franke, *Annalen*, 1965, **681**, 10.

<sup>3</sup> G. Paiaro and R. Palumbo, *Angew. Chem.*, 1963, **75**, 861.

<sup>4</sup> B. Bogdanovic, M. Kröner, and G. Wilke, *Annalen*, 1966, **699**, 1; H. Dietrich and H. Schmidt, *Naturwiss.*, 1965, **52**, 301; K. Jonas, P. Heimbach, and G. Wilke, *Angew. Chem. Internat. Edn.*, 1968, **7**, 949.

<sup>5</sup> G. Paiaro, N. Netto, A. Musco, and R. Palumbo, *Ric. Sci., Rend. Sez. A.*, 1965, **8** (6), 1441.

<sup>6</sup> E. Kuljian and H. Frye, *Z. Naturforsch.*, 1965, **19b**, 651; M. Genas, T. Rüll, and G. Le Strat, *Compt. Rend.*, 1970, **271C**, 1400.

<sup>7</sup> G. McCauley and H. Frye, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 21.

<sup>8</sup> B. W. Cook, R. G. J. Miller, and P. F. Todd, *J. Organometallic Chem.*, 1969, **19**, 421.

<sup>9</sup> L. I. Zakharkin and V. V. Korneva, *Doklady Akad. Nauk SSSR*, 1960, **132**, 1078; S. Kuribayashi, N. Yasuoka, T. Mitsui, H. Takahashi, and M. Yamaguchi, *Bull. Chem. Soc. Japan*, 1964, **37**, 1242; K. C. Untch and D. J. Martin, *J. Amer. Chem. Soc.*, 1965, **87**, 3518.

<sup>10</sup> R. Hüttel, H. Reinheimer, and H. Dietl, *Chem. Ber.*, 1966, **99**, 462.

<sup>11</sup> W. Fröhlich, Ph.D. Thesis, University of Munich, quoted in E. O. Fischer and H. Werner, *Angew. Chem.*, 1963, **75**, 62; *Internat. Edn.*, 1963, **2**, 85.

TABLE I  
 Analytical data

Complex	M.p. (°C) <sup>a</sup>	Found (calculated) values					
		C	H	O	P	Ru	M
(II) HRu <sub>3</sub> (CO) <sub>9</sub> (C <sub>12</sub> H <sub>15</sub> )	138	35.4 (35.15)	2.6 (2.25)	20.3 (20.1)		41.8 (42.5)	718 <sup>o</sup> (717)
(III) HRu <sub>3</sub> (CO) <sub>9</sub> (C <sub>12</sub> H <sub>17</sub> )	150	35.25 (35.1)	2.6 (2.5)	20.6 (20.05)		41.7 (42.3)	719 (719)
(IV) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>24</sub> H <sub>31</sub> )	194	44.5 (45.05)	4.25 (4.5)	14.35 (13.55)		37.1 (36.9)	824 (823)
(V) Ru <sub>4</sub> (CO) <sub>10</sub> (C <sub>12</sub> H <sub>16</sub> )	143	31.35 (31.2)	1.6 (1.9)	19.05 (18.9)		48.15 (48.0)	845 <sup>o</sup> (846)
(VI) HRu <sub>3</sub> (CO) <sub>6</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OMe) <sub>3</sub> ] <sub>3</sub>	190—195	31.85 (32.2)	4.75 (4.35)	23.9 (23.85)	9.2 (9.25)	30.5 (30.35)	1004 (1005)
(VII) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OMe) <sub>3</sub> ] <sub>2</sub>	145—150	33.25 (33.0)	3.95 (3.75)	22.35 (22.85)	5.45 (6.8)	35.05 (33.6)	911 (909)
(VIII) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OCH <sub>2</sub> ) <sub>3</sub> CEt] <sub>2</sub>	190	39.4 (37.65)	4.0 (4.15)	19.4 (21.05)	5.95 (6.15)	31.0 (30.85)	
(IX) HRu <sub>3</sub> (CO) <sub>6</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OCH <sub>2</sub> ) <sub>3</sub> CEt] <sub>3</sub>	135	37.4 (38.5)	4.45 (4.65)	21.8 (21.4)	8.2 (8.25)		

<sup>a</sup> With decomposition, except for (II). <sup>b</sup> Mass spectrometry. <sup>o</sup> See Table 5.

of these structure determinations will be published separately,<sup>12</sup> but some preliminary details have already appeared.<sup>13</sup> The properties and reactions of these complexes are best discussed in the light of these structures.

 TABLE 2  
 Carbonyl stretching frequencies <sup>a</sup>

Complex	$\nu(\text{CO}), \text{cm}^{-1}$
(II) HRu <sub>3</sub> (CO) <sub>9</sub> (C <sub>12</sub> H <sub>15</sub> )	2096m, 2070s, 2045s, 2027s, 2015m, 2007s, 1995w, 1973w
(III) HRu <sub>3</sub> (CO) <sub>9</sub> (C <sub>12</sub> H <sub>17</sub> )	2087m, 2058s, 2033s, 2017s, 2009w, 2002m, 1994w, 1990w, 1982w, 1972w
(IV) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>24</sub> H <sub>31</sub> )	2054m, 2018s, 1998w, 1977m, 1965m
(V) Ru <sub>4</sub> (CO) <sub>10</sub> (C <sub>12</sub> H <sub>16</sub> )	2075m, 2034s, 2006w, 1992m, 1975w, 1956w
(VI) HRu <sub>3</sub> (CO) <sub>6</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OMe) <sub>3</sub> ] <sub>3</sub>	2036s, 2012s, 1976m, 1964m, 1921w
(VII) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OMe) <sub>3</sub> ] <sub>2</sub>	2057m, 2018s, 1983m, 1965w, 1957w
(VIII) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OCH <sub>2</sub> ) <sub>3</sub> CEt] <sub>2</sub>	2077m, 2040s, 2023s, 1995m, 1978m
(IX) HRu <sub>3</sub> (CO) <sub>6</sub> (C <sub>12</sub> H <sub>15</sub> )[P(OCH <sub>2</sub> ) <sub>3</sub> CEt] <sub>3</sub>	2050s, 2018s, 2010s, 1970s
(X) HRu <sub>3</sub> (CO) <sub>8</sub> (C <sub>12</sub> H <sub>15</sub> )(PMe <sub>2</sub> Ph)	2974s, 2053w, 2035s, 2016s, 1989m, 1980m, 1966m, 1956w
(XI) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>12</sub> H <sub>15</sub> )(PMe <sub>2</sub> Ph) <sub>2</sub>	2040m, 2004s, 1965m, 1954w, 1944w

<sup>a</sup> Cyclohexane solution, except for (VIII) (chloroform).

The major product from these reactions forms bright yellow, air-stable crystals, shown to have structure (II). The mode of attachment of the hydrocarbon in (II) bears a striking resemblance to that of the PhCC<sub>6</sub>H<sub>4</sub> moiety in the complex HRu<sub>3</sub>(CO)<sub>9</sub>(PhCC<sub>6</sub>H<sub>4</sub>) (IIa), obtained from reactions between phenyl-lithium and Ru<sub>3</sub>(CO)<sub>12</sub>.<sup>14</sup> As can be seen from the diagrammatic

<sup>12</sup> A. Cox and P. Woodward, *J. Chem. Soc. (A)*, 1971, 3599; R. Belford, H. P. Taylor, and P. Woodward, paper in preparation.

<sup>13</sup> M. I. Bruce, M. A. Cairns, A. Cox, M. Green, M. D. H. Smith, and P. Woodward, *Chem. Comm.*, 1970, 735; R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159.

representations, the geometries of the bonded C<sub>3</sub> units are almost the same, and in both cases the structural parameters could be interpreted in terms of an extended mesomeric heterocyclic (C<sub>3</sub>Ru<sub>2</sub>) system, stabilised by the allyl-Ru<sup>3</sup>  $\pi$  bond. Complex (II) contains the largest carbocycle yet to be found associated with a metal cluster.

The proton n.m.r. spectrum of complex (II) shows complex resonances in the olefinic (6H) and aliphatic

 TABLE 3  
 Proton n.m.r. spectra

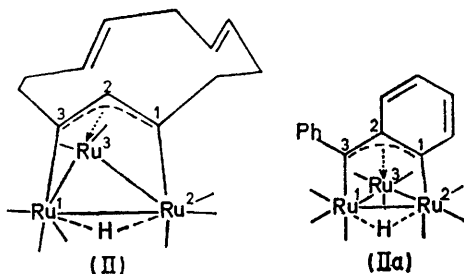
Complex	Chemical shift ( $\tau$ ) <sup>a</sup>	Relative intensity	Assignment (coupling constants, Hz)
(II) HRu <sub>3</sub> (CO) <sub>9</sub> (C <sub>12</sub> H <sub>15</sub> )	3.81d 4.67	1 2	C <sup>2</sup> -H (2.5)
	6.8—8.5 30.24d	12 1	Ru-H (2.5)
(IV) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>24</sub> H <sub>31</sub> )	4.44t 4.65 5.52	1 2 2	
	7.0—8.6 32.83d	29 1	Ru-H (21.0)
(V) Ru <sub>4</sub> (CO) <sub>10</sub> (C <sub>12</sub> H <sub>16</sub> )	4.02s 6.22t 7.20 8.20	1 1 6 8	C <sup>2</sup> -H C <sup>2</sup> -H
(VI) HRu <sub>3</sub> (CO) <sub>6</sub> (C <sub>12</sub> H <sub>15</sub> )-[P(OMe) <sub>3</sub> ] <sub>3</sub>	3.32m,br 4.66m,br 6.54td 7.0—9.0 30.01tt	1 2 27 12 1	C <sup>2</sup> -H P-OMe (12) Ru-H (14)
(VII) HRu <sub>3</sub> (CO) <sub>7</sub> (C <sub>12</sub> H <sub>15</sub> )-[P(OMe) <sub>3</sub> ] <sub>2</sub>	3.00s,br 4.62s,br 6.57dd 7.0—8.5 29.91tt	1 2 18 12 1	C <sup>2</sup> -H P-OMe (12) Ru-H (13)

<sup>a</sup> All signals are complex multiplets unless otherwise indicated.

(8H) regions, the overall line shapes of which change during decoupling experiments. However, the latter yield no further structural information. The only other

<sup>14</sup> A. W. Parkins, E. O. Fischer, G. Huttner, and D. Regler, *Angew. Chem.*, 1970, 82, 635; *Internat. Edn.*, 1970, 9, 633.

signals present are doublets at  $\tau$  3.81 and 30.24, which can be shown by double resonance experiments to be coupled together ( $J$  2.5 Hz). Inspection of the structure shows that H<sup>2</sup> is the only proton on the C<sub>12</sub> ring which is unlikely to be coupled to any other ring protons.



Selected parameters:

	(II)	(IIa)
Ru <sup>1</sup> -Ru <sup>2</sup>	2.921	2.914 Å
Ru <sup>1</sup> -Ru <sup>3</sup>	2.773	2.773
Ru <sup>2</sup> -Ru <sup>3</sup>	2.779	2.776
Ru <sup>1</sup> -C <sup>3</sup>	2.04	2.08
Ru <sup>2</sup> -C <sup>1</sup>	2.04	2.10
Ru <sup>3</sup> -C <sup>2</sup>	2.15	2.36

The metal-bonded hydrogen atom probably bridges Ru<sup>1</sup> and Ru<sup>2</sup>. This follows from the chemical shift, which lies in the region associated with bridging hydrogen atoms, rather than with terminal protons. Thus for the same metal, values for terminal protons are  $\tau$  ca. 16, whereas hydrogen atoms bridging two metal atoms resonate at considerably higher field. Two examples are for chromium, e.g.  $(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$  at  $\tau$  15.95,<sup>15</sup> and  $[\text{HCr}_2(\text{CO})_{10}]^-$  at 29.17,<sup>16</sup> and for ruthenium in H<sub>2</sub>Ru<sub>4</sub>(CO)<sub>13</sub> at  $\tau$  19.1,<sup>17</sup> and in H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> at  $\tau$  27.6.<sup>17</sup> It is of some interest that the similar proton in complex (IIa) resonates at  $\tau$  30.2. In addition, in several recent instances, a longer metal-metal bond has been used as evidence for the location of a bridging hydrogen atom.<sup>18</sup>

A further point of interest concerning the proton n.m.r. spectrum of complex (II) is the small coupling between the metal-bonded proton and H<sup>2</sup>. No previous examples of this type of coupling (H-Ru-C-C-H), which is probably facilitated by the presence of the metal-carbon  $\sigma$  bonds, have been reported.

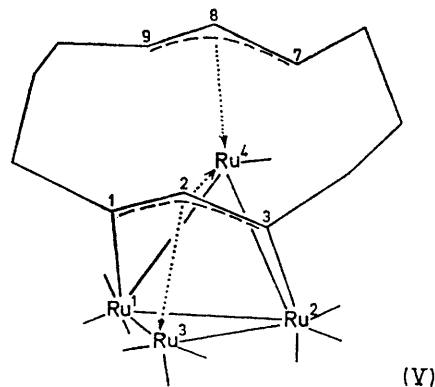
Chemical confirmation of the monocyclic C<sub>12</sub> ring was obtained by hydrogenation of complex (II). This reaction afforded cyclododecane, and the cluster hydride H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub>. In the hope that further information concerning the location of the double bonds could be obtained, a carbonylation experiment was attempted. However, the products were Ru(CO)<sub>5</sub>, and complex organic oils which could not be identified.

Treatment of complex (II) with Ru<sub>3</sub>(CO)<sub>12</sub> in a separate experiment afforded complex (V), which no longer shows a metal-hydrogen resonance in its proton n.m.r. spectrum. A reaction between complex (II) and

Fe<sub>2</sub>(CO)<sub>9</sub> did not afford any evidence for the formation of an analogous FeRu<sub>3</sub> complex. The structural similarities between complexes (II) and (V) suggest that the latter is formed by a formal incorporation of a fourth ruthenium atom into the cluster. This reaction is probably facilitated by interaction of one of the uncoordinated double bonds of the C<sub>12</sub> system in (II) with Ru<sub>3</sub>(CO)<sub>12</sub>.

Apart from complex resonances in the aliphatic and olefinic regions, the proton n.m.r. spectrum of (V) exhibited a singlet at  $\tau$  4.02 and a triplet at  $\tau$  6.22. These may be assigned to the central protons of the two allylic systems, namely H<sup>3</sup> and H<sup>8</sup>, respectively. The latter is coupled to the protons on each of the outer carbon atoms, H<sup>7</sup> and H<sup>9</sup>.

The unprecedented feature of the structure of complex (V) is the central C<sub>3</sub> unit which is associated with all four metal atoms. The bonding is *via* two metal-carbon  $\sigma$  bonds from C<sup>1</sup> to Ru<sup>1</sup>, and from C<sup>3</sup> to Ru<sup>2</sup>, as already found in complex (II). The other two metal atoms interact with the C<sub>3</sub> unit by means of a  $\pi$ -type bond. Formal electron counts give Ru<sup>1</sup> and Ru<sup>2</sup> ten electrons each from the attached ligands, and the metal-metal bonds. Neglecting the bridging C<sub>3</sub> unit, Ru<sup>3</sup> and Ru<sup>4</sup> receive eight and seven electrons, respectively,



from the same considerations. It is unlikely that the C<sub>3</sub> unit would supply *five*  $\pi$ -type electrons to enable the EAN rule to be conformed with, and we prefer to consider that this group acts as a conventional  $3\pi$  donor. It is possible to construct three-centre molecular orbitals from the three bonding, non-bonding, and anti-bonding orbitals of the allyl group, and bonding  $d$  orbitals of the appropriate symmetry from the two metal atoms. The resulting MO's consist of three bonding orbitals, which accept six electrons, and a fourth orbital, which is essentially non-bonding, and remains unoccupied.

The nature of complexes (III) and (IV) has not been completely resolved. However the similarity of the infrared spectra of complexes (II) and (III), together with their proton n.m.r. spectra, suggest that (III) has a similar structure to (II). It is likely that as a result

<sup>15</sup> T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

<sup>16</sup> R. G. Hayter, *J. Amer. Chem. Soc.*, 1966, **88**, 4376.

<sup>17</sup> B. F. G. Johnson, R. D. Johnson, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. (A)*, 1968, 2856.

<sup>18</sup> M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Amer. Chem. Soc.*, 1968, **90**, 7135; M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Comm.*, 1970, 458.

of the hydrogen-migration and -isomerisation reactions that occur in the formation of these complexes, only minor differences, such as the saturation of one of the unco-ordinated double bonds, exist between these two complexes.

TABLE 4  
Calculated masses and relative intensities

Nominal mass	Multiplicity	Spread (p.p.m.)	Accurate mass	Relative abundance
(a) Ru <sub>3</sub>				
288	1		287.7228	0.14
290	1		289.7205	0.14
291	1		290.7211	0.96
292	2	4.2	291.7193	1.01
293	2	6.7	292.7201	1.95
294	4	13	293.7192	5.28
295	3	6.6	294.7178	5.41
296	6	20	295.7183	12.1
297	5	8.2	296.7175	20.4
298	7	17	297.7166	24.1
299	6	15	298.7170	39.1
300	8	15	299.7159	53.6
301	6	15	300.7156	57.4
302	7	15	301.7156	86.6
303	5	8.6	302.7147	87.8
304	6	18	303.7149	92.3
305	3	4.7	304.7150	100.0
306	4	12	305.7142	78.5
307	2	4.7	306.7156	61.1
308	2	3.1	307.7143	57.3
309	1		308.7164	14.7
310	1		309.7152	27.3
312	1		311.7163	5.34
(b) Ru <sub>4</sub>				
384	1		383.6304	0.01
386	1		385.6281	0.01
387	1		386.6287	0.09
388	2	3.2	387.6269	0.09
389	2	5.0	388.6275	0.20
390	4	9.4	389.6267	0.60
391	3	5.0	390.6254	0.74
392	7	18	391.6257	1.66
393	6	9.4	392.6250	3.17
394	9	16	393.6240	4.34
395	9	15	394.6242	7.81
396	13	15	395.6233	12.5
397	11	17	396.6228	16.5
398	15	18	397.6227	26.7
399	13	14	398.6219	35.4
400	16	23	399.6216	45.2
401	13	13	400.6214	61.4
402	15	18	401.6207	71.9
403	11	15	402.6206	82.6
404	13	14	403.6203	98.5
405	9	14	404.6198	95.3
406	9	14	405.6200	100.0
407	6	8.7	406.6197	92.7
408	7	16	407.6196	75.4
409	3	3.5	408.6202	64.2
410	4	8.6	409.6193	46.9
411	2	3.5	410.6209	25.8
412	2	2.3	411.6197	24.1
413	1		412.6218	4.41
414	1		413.6206	8.18
416	1		415.6217	1.20

The mass spectrum of complex (IV), which can also be obtained in small amount from a reaction between complex (II) and excess CDT, shows a cut-off at  $m/e$  162, suggesting that two C<sub>12</sub> ligands are involved.

Reactions of complex (II) with phosphines or phosphites resulted in substitution of up to three carbonyl groups by the phosphorus ligands. These new com-

plexes retained the hydrocarbon ligand. Thus with dimethylphenylphosphine, compounds with one and two phosphines were prepared. With the phosphites P(OMe)<sub>3</sub> and P(OCH<sub>2</sub>)<sub>3</sub>CEt, the resulting complexes had two and three ligands. It is likely for steric reasons that each ligand is attached to a different metal atom, although it was not possible to determine the precise stereochemistry. The proton n.m.r. spectra of the P(OMe)<sub>3</sub> complexes suggest that the first two phosphite molecules bond to similar metal atoms (the methyl resonances appear as two doublets at  $\tau$  6.57, separated by only 1.6 Hz), whereas the third is attached to a metal atom in a rather different environment (a triplet of doublets, separated by 1.4 and 3.0 Hz). In complexes (VI) and (VII), the Ru-*H* resonance appears as a triplet of triplets, lending support to the idea of two phosphites in similar environments, *i.e.* attached to Ru<sup>1</sup> and Ru<sup>2</sup>, and also to the proposed location of the metal-bonded proton. In no case was the hydrocarbon displaced to give either Ru<sub>3</sub>(CO)<sub>9</sub>(PR<sub>3</sub>)<sub>3</sub> or Ru(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub> complexes.

The mass spectra of all the compounds discussed are complex and difficult to interpret. In general, more or less abundant hydrocarbon ions are found at selected  $m/e$  values between  $m/e$  39 and 164, probably being formed by the breakdown of the ionised hydrocarbon ligand. Between  $m/e$  220—400 lie a series of doubly-charged ions, which appear as envelopes of individual

TABLE 5  
High-resolution mass spectra: observed and calculated peak masses

	Observed	Calculated <sup>a</sup>	
		C <sub>12</sub> H <sub>15</sub>	C <sub>12</sub> H <sub>16</sub>
(a) HRU <sub>3</sub> (CO) <sub>9</sub> (C <sub>12</sub> H <sub>15</sub> )			
	715.7993	715.7977	
	716.7958	716.7978	716.8055
	717.7978	717.7970	717.8056
	718.7992	718.7984	718.8048
	719.7975	719.7971	719.8062
	720.7964	720.7992	720.8049
	721.7965	721.7980	721.8081
	722.7955		722.8058
(b) Ru <sub>4</sub> (CO) <sub>10</sub> (C <sub>12</sub> H <sub>16</sub> )			
	844.6914	844.6866	844.6942
	845.6916	845.6862	845.6944
	846.6899	846.6861	846.6941
	847.6931	847.6867	847.6939
	848.6952	848.6858	848.6945
	849.6948	849.6875	849.6936

<sup>a</sup> Calculated values for either a C<sub>12</sub>H<sub>15</sub> or C<sub>12</sub>H<sub>16</sub> hydrocarbon ligand, *i.e.* in the case of complex (II), the total hydrogens are 16 or 17, respectively.

peaks separated by half m.u. intervals. These do not generally correspond to the parent ion, but may be related to other ions formed by loss of CO, hydrogen, and possibly olefin. Singly charged ions generally extend from  $m/e$  400 to the parent ion cluster, and each envelope is separated from the next by between 26 and 30 m.u. The most intense peak in each cluster is listed in the Experimental section. The complex envelopes of peaks were analysed with the help of the computed

patterns for Ru<sub>3</sub> and Ru<sub>4</sub> groups (Table 4). The identities of the molecular ions of complexes (II) and (V) were confirmed by high-resolution measurements on several peaks of the cluster (Table 5).

#### EXPERIMENTAL

*Reaction of CDT with Ru<sub>3</sub>(CO)<sub>12</sub>.*—A mixture of Ru<sub>3</sub>(CO)<sub>12</sub> (1.0 g, 1.56 mmol) and all-*trans*-CDT (750 mg, 4.6 mmol) was refluxed in light petroleum (b.p. 80–100°) for 30 h, the progress of the reaction being followed by infrared spectroscopy [ $\nu$ (CO) region]. Evaporation, and extraction of the residue with boiling cyclohexane, was followed by chromatography (Florisil, 1-m column) of the filtered extract. Elution with pentane–benzene mixtures gave three fractions. Complex (II) was eluted first, and recrystallisation (pentane) gave yellow-orange crystals (720 mg, 64%). The complex could also be purified by sublimation (90°/0.1 mm). The second fraction contained (II) and (III), which were separated by a second chromatography, followed by recrystallisation (pentane) to give small dark orange crystals of (III) (2 mg, 1%). The third fraction contained (IV) and (V) (by infrared spectroscopy), but

parent ion at  $m/e$  168]. The residue from the sublimation was bright yellow, and identified as H<sub>4</sub>Ru<sub>4</sub>(CO)<sub>12</sub> by comparison with an authentic sample.

*Reactions of Complex (II).*—(a) *With trimethyl phosphite.* Refluxing a mixture of trimethyl phosphite and complex (II) in cyclohexane until no further change occurred in the  $\nu$ (CO) region of the infrared spectrum (*ca.* 4 h) afforded an orange reaction mixture. Chromatography on Florisil resulted in the isolation of orange HRu<sub>3</sub>(CO)<sub>6</sub>(C<sub>12</sub>H<sub>15</sub>)[P(OMe)<sub>3</sub>]<sub>3</sub> (VI) (20%) (eluted with 3 : 7 ether–light petroleum); and bright yellow HRu<sub>3</sub>(CO)<sub>7</sub>(C<sub>12</sub>H<sub>15</sub>)[P(OMe)<sub>3</sub>]<sub>2</sub> (VII) (10%) (eluted with 6 : 4 ether–light petroleum).

(b) *With P(OCH<sub>2</sub>)<sub>3</sub>CET.* A similar reaction with the cage phosphite was carried out for 2 h. Chromatography of the yellow reaction mixture afforded yellow HRu<sub>3</sub>(CO)<sub>7</sub>(C<sub>12</sub>H<sub>15</sub>)[P(OCH<sub>2</sub>)<sub>3</sub>CET]<sub>2</sub> (VIII) (15%) (eluted with 10% ether–light petroleum), and yellow HRu<sub>3</sub>(CO)<sub>6</sub>(C<sub>12</sub>H<sub>15</sub>)[P(OCH<sub>2</sub>)<sub>3</sub>CET]<sub>3</sub> (IX) (from ether). The reverse order of elution (compared with that of the trimethyl phosphite products) is notable.

(c) *With dimethylphenylphosphine.* Complex (II) was refluxed in cyclohexane with a large excess of the phosphine for 1 h. Ether eluted two complexes, apparently the

TABLE 6  
Reactions of CDT with Ru<sub>3</sub>(CO)<sub>12</sub>

CDT (mg)	Ru <sub>3</sub> (CO) <sub>12</sub> (mg)	Solvent (ml) <sup>a</sup>	Time (h)	Yields of complexes in mg (%)			
				(II)	(III)	(IV)	(V)
<i>all-trans</i>							
100	200	15	52	64 (30)	<i>b</i>	<i>I.r.</i> <sup>c</sup>	<i>I.r.</i>
1000	750	30	30	720 (64)	2 (1)		
1000	750	30	100	200 (10)		40 (5)	30 (3)
2250	3000	90	26	1630 (50)		18 (1)	17 (0.6)
750	1000	30	100	180 (10)	<i>I.r.</i>	60 (4)	
<i>all-cis</i>							
100	200	15	52	70 (32)		<i>I.r.</i>	<i>I.r.</i>
<i>cis,cis,trans</i>							
100	200	15	52	45 (20)		<i>I.r.</i>	<i>I.r.</i>

<sup>a</sup> Solvent was light petroleum (b.p. 80–100°) in all cases, refluxing for the time stated. <sup>b</sup> Infrared spectrum indicated that (III) was present after 20 h. <sup>c</sup> *I.r.* = Detected by infrared spectrum, but not isolated.

these complexes were more readily obtained from a similar mixture of Ru<sub>3</sub>(CO)<sub>12</sub> and CDT which had been heated (100 h) until there was no further change in the infrared spectrum. Chromatography afforded (II) (200 mg, 10%) as above; a dark yellow fraction, which gave yellow-brown crystals of (IV) (40 mg, 5%) (pentane); and a third fraction (benzene) which afforded dark red plate-like crystals of (V) (30 mg, 3%) (pentane–diethyl ether). Both complexes sublimed with some decomposition.

Under different conditions, varying amounts of these complexes were obtained. In cases where the total yields are low, there was no recovery of Ru<sub>3</sub>(CO)<sub>12</sub>. After extraction with organic solvents, including acetone, much intractable, dark-coloured material remained, which was not further investigated. Representative experiments are summarised in Table 6.

*Reduction of Complex (II) (with J. P. A. BROWN).*—Complex (II) (100 mg, 0.155 mmol) in light petroleum (b.p. 30–40°) was hydrogenated (100°/100 atm/24 h). Evaporation and sublimation afforded a white solid, identified as cyclododecane [m.p. 60° (lit.,<sup>19</sup> 60.5°); mass spectrum:

yellow mono- (X), and the orange disubstituted (XI) products [Found: (X): C, 43.45; H, 4.2; O, 13.95; P, 3.8; Ru, 33.9. Calc. for C<sub>28</sub>H<sub>27</sub>O<sub>8</sub>PRu<sub>3</sub>: C, 40.5; H, 3.6; O, 15.4; P, 3.75; Ru, 36.75%. Found for (XI): C, 47.1; H, 4.95; O, 12.8. Calc. for C<sub>35</sub>H<sub>38</sub>O<sub>7</sub>P<sub>2</sub>Ru<sub>3</sub>: C, 44.7; H, 4.35; O, 11.9%].

*Mass Spectra.*—The ions present in the mass spectra of several of the complexes are listed under two types. Hydrocarbon ions, mainly found below  $m/e$  170, and usually single peaks, and singly-charged clusters of peaks resulting from the various isotopic contributions of the Ru<sub>3</sub> or Ru<sub>4</sub> group. Asterisked peaks also appear at lower  $m/e$  values as their doubly-charged counterparts.

*Complex (II):* hydrocarbon ions at  $m/e$  54, 55, 67, 79, 91, 93, 108, 121, 133, 147, 162; cluster ions centred on  $m/e$  404, 428, 455\*, 485\*, 515\*, 544\*, 572\*, 602\*, 631\*, 661, 689, 718.

*Complex (III):* hydrocarbon ions at  $m/e$  41, 54, 67, 79, 81, 91, 93, 121, 133, 160, 162, 164; cluster ions centred on  $m/e$  406, 458\*, 488\*, 517\*, 546\*, 576\*, 604\*, 634\*, 664, 691, 720.

*Complex (IV):* hydrocarbon ions at  $m/e$  41, 43, 54, 55, 67, 79, 80, 81, 91, 93, 105, 121, 133, 162, 164, 166; cluster

<sup>19</sup> L. Ruzicka, M. Stoll, H. Huyser, and H. G. Bockanooger, *Helv. Chim. Acta*, 1930, **13**, 1152.

ions centred on  $m/e$  431\*, 458\*, 488\*, 517\*, 547\*, 575\*, 614\*, 651\*, 682, 712, 739, 768, 796, 824.

*Complex (V)*: hydrocarbon ions at  $m/e$  55, 57, 69, 71, 81, 83, 85, 94, 96, 108, 110, 122, 124, 136, 138, 140, 150, 164; cluster ions centred at  $m/e$  429, 452, 479, 505\*, 529\*, 555\*, 587\*, 616\*, 643\*, 672\*, 701\*, 730\*, 759\*, 789\*, 815\*, 844.

*Complex (VI)*: hydrocarbon ions at  $m/e$  63, 79, 93, 124, 160, 162, 164, 168; cluster ions centred at  $m/e$  487\*, 518\*,

548\*, 580\*, 610\*, 642\*, 673\*, 704\*, 733\*, 764\*, 794\*, 824\*, 858\*, 888\*, 918, 945, 976, 1006.

*Complex (VII)*: hydrocarbon ions at  $m/e$  47, 63, 67, 79, 93, 109, 124, 158, 160, 162; cluster ions centred at  $m/e$  488\*, 520\*, 549\*, 582\*, 612\*, 642\*, 674\*, 706\*, 736\*, 765\*, 795, 825, 853, 883, 911.

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