Hydrocarbon Complexes of Ruthenium. Part I. Formation of 1,2,3,3a,6a-η-1,4,5,6-Tetrahydropentalenyl Complexes from Organo-silyl- and -germyl-(carbonyl)ruthenium Compounds

By **Selby A. R. Knox, Richard P. Phillips,** and **F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

all-*trans*-Cyclododeca-1,5,9-triene undergoes a ring contraction reaction with tetracarbonylbis(trimethylgermyl)-ruthenium to give the tetrahydropentalenylruthenium complexes $[Ru(GeMe_3)(CO)_2(C_8H_9)]$ and $[Ru_2(GeMe_3)(\mu\text{-}GeMe_2)_2(CO)_4C_8H_9]$, and the pentalene complex $[Ru_2(GeMe_3)_2(CO)_4(C_8H_6)]$. The two tetrahydropentalenyl complexes are also formed in the reaction between cyclo-octa-1,5-diene and tetracarbonylbis(trimethylgermyl)-ruthenium, but the major product of this reaction is the cyclo-octa-1,5-diene complex $[Ru(GeMe_3)_2(CO)_2(C_8H_{12})]$. Cyclododeca-1,5,9-triene also undergoes ring contraction on reaction with $Ru(SiMe_3)_2(CO)_4$, forming $[Ru(SiMe_3)(CO)_2(C_8H_9)]$ and $[Ru_2(CO)_6(C_8H_{10})]$. Similar reactions occur with the binuclear ruthenium compounds $[Ru(CO)_4(MMe_3)]_2$ (M = Si or Ge).

REACTIONS of cyclic polyolefins with the carbonyl complexes of metals of the iron triad have been a prolific source of hydrocarbon complexes of various structural types,[1] many of which are fluxional.[2] The structural and dynamic properties of a particular type of complex are markedly dependent upon the nature of both the metal and its ligands. The availability [3,4] of the compounds $[(R_3M)_2M'(CO)_4]$ (M = Si, Ge, or Sn; M′ = Fe, Ru, or Os) and $[R_3MM'(CO)_4]_2$ (M′ = Ru or Os) presented an opportunity to extend this field in a new direction by investigating reactions of these species with cyclic polyolefins. New hydrocarbon complexes containing the formally one-electron ligands R_3M would be expected to show considerable differences in structure from complexes derived from the parent carbonyls.

Physical and spectroscopic data for some Group IVB carbonylruthenium compounds

Complex	Colour	M.p. (t/°C) (B.p. at 10^{-2} mmHg)	ν_{CO}/cm^{-1} *	τ †
$[Ru(GeMe_3)(CO)_2(C_8H_9)]$	Yellow	(*ca.* 60)	2004s, 1949s	5·02d (2H, *J* 2·3), 5·19t (1H, *J* 2·3), 7·64m (6H, 9·60s (9H)
$[Ru(SiMe_3)(CO)_2(C_8H_9)]$	Yellow	(*ca.* 60)	2006s, 1949s	5·14d (2H, *J* 2·5), 5·34t (1H, *J* 2·5), 7·66m (6H), 9·62s (9H)
$[Ru_2(GeMe_3)(GeMe_2)_2(CO)_4(C_8H_9)]$	Yellow	73—74	2041m, 1988s, 1979s, 1943m	5·49d (2H, *J* 2·5), 6·34t (1H, *J* 2·5), 7·22m (6H), 8·96s (6H), 9·11s (6H), 9·63s (9H)
$[Ru(GeMe_3)_2(CO)_2(C_8H_{12})]$	Colourless	138 (decomp.)	2021w, 2010w, 1977w, 1959s	5·75s (4H), 7·80 (8H), 9·93s (18H).
$[Ru(GeMe_3)_2(CO)_2\{P(OMe)_3\}_2]$	Colourless	156—160 (decomp.)	1953s	6·63m (18H), 9·80s (18H)

* Hexane solution; Perkin-Elmer 257 spectrophotometer. † $CDCl_3$ solution; *J* in Hz.

Herein we describe reactions of trimethylsilyl- and trimethylgermyl-(carbonyl)ruthenium complexes (I and II; M = Si or Ge) with all-*trans*-cyclododeca-1,5,9-triene (cdt) and with cyclo-octa-1,5-diene (cod).[5] Organotin complexes of type (I), those of type (II) being unknown,† appear to react similarly to their organogermanium analogues, but very low yields of product are obtained, and these have not been investigated extensively.

Tetracarbonylbis(trimethylgermyl)ruthenium (I; M = Ge) reacts with cdt in heptane at reflux to give four air-stable products identified as the known metal cluster complex $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$,[4c] two 1,2,3,3a,6a-η-1,4,5,6-tetrahydropentalenylruthenium complexes (III; M = Ge) and (IV), and the pentalene complex (V), whose molecular structure and synthesis by a different route have been reported.[6] Both (III; M = Ge) and (IV) exhibit molecular ions in their mass spectra, which also show ions at *m/e* 105 ($C_8H_9^+$). The ^1H n.m.r. spectra of both complexes (Table) give conclusive evidence for the presence of the 1,2,3,3a,6a-η-1,4,5,6-tetrahydropentalenyl ligand. Thus for (III; M = Ge) the six aliphatic protons are observed as a multiplet at τ 7·64, and the three cyclopentadienyl ring protons appear as an essentially first-order doublet (τ 5·02; 2H) and triplet (τ 5·19; 1H). The structure of (IV) is closely related to those of the cluster complexes $[Ru(CO)_3(MMe_3)(\mu\text{-}MMe_2)]_2$ (M = Si, Ge, or Sn), two of which have been the subject

---

† The complex $[Me_3SnRu(CO)_4]_2$ has recently been prepared in this laboratory by Miss J. D. Edwards.

[1] M. A. Bennett, *Chem. Rev.*, 1962, **62**, 611.

[2] F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257.

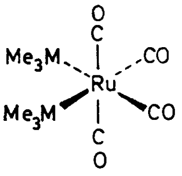
[3] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2758; J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *ibid.*, 1967, 264.

[4] (*a*) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559; (*b*) 1970, 3147; (*c*) 1971, 2874.

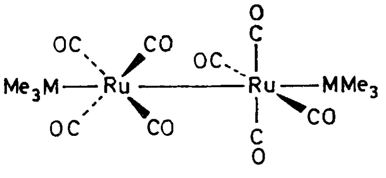
[5] S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1973, 1227.

[6] A. Brookes, J. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 587.

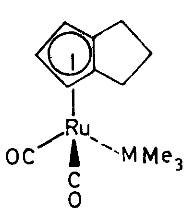
of single crystal *X*-ray diffraction studies.[7,8] The presence of non-equivalent bridging dimethylgermyl ligands in (IV) is indicated by ^{1}H n.m.r. signals at τ 8·96 (6H, s) and 9·11 (6H, s); the signal for the terminal trimethylgermyl group occurs at τ 9·63 (9H, s). Similar chemical shifts have been observed in the spectra of the complexes $[Ru(CO)_3(MMe_3)(\mu\text{-}MMe_2)]_2$.[3,4]



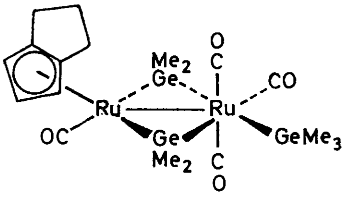
(I) M=Si or Ge



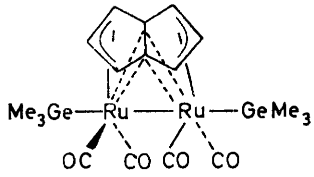
(II) M=Si or Ge



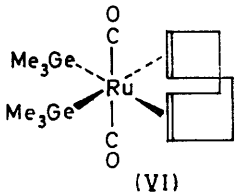
(III) M=Si or Ge



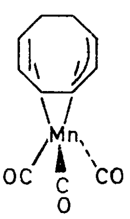
(IV)



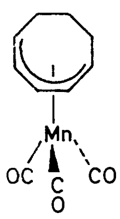
(V)



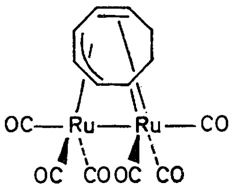
(VI)



(VII)



(VIII)



(IX)

The unusual transformation of the C_{12} ring of cdt to afford the products (III; M = Ge) and (IV) led us to carry out experiments designed to establish that these compounds with their C_8 ligands did not originate from some other source. Heating (I; M = Ge) in heptane alone yielded only small amounts of $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ and no trace of the compounds (III; M = Ge), (IV), or (V). Further evidence against the solvent as a source of the co-ordinated C_8 hydrocarbons was provided by high resolution g.l.c., which showed the heptane used to be free of any C_8 hydrocarbon (one part in 2×10^4 would have been detected). The cdt was similarly found to have no hydrocarbon impurities above this limit of detection.

The mechanism by which the C_{12} hydrocarbon cdt reacts with (I; M = Ge) to give the C_8 hydrocarbon complexes (III; M = Ge), (IV), and (V) must necessarily be complicated. It is worth recalling that cyclododecatriene itself is formed by oligomerising the C_4 hydrocarbon butadiene with low-valent nickel complexes.[9]

Formation of tetrahydropentalenyl complexes from monocyclic unsaturated C_8 hydrocarbons has been observed previously.[10-13] This suggested that such hydrocarbons, or their complexes, might be intermediates in the foregoing reaction. Accordingly, (I; M = Ge) was treated with cod in heptane at reflux. Complexes (III; M = Ge) and (IV) were indeed formed, but in addition the cyclo-octa-1,5-diene complex (VI) was obtained (30% yield) as a colourless crystalline solid.

Although isomerisation of cyclo-octa-1,5-diene to the 1,3-isomer is common in reactions with metal carbonyls, the n.m.r. spectrum of (VI) shows only one signal for the olefinic protons, in line with co-ordination of cyclo-octa-1,5-diene. Only one signal for the Me_3Ge protons is observed, and in the i.r. spectrum carbonyl bands at 2010w and 1959s cm^{-1} are as expected for the symmetric and asymmetric stretching modes of two mutually *trans* CO groups. Additional weak bands at 2021 and 1977 cm^{-1} indicate that a small amount of a *cis*-dicarbonyl isomer of (VI) co-exists with the *trans*-form. The n.m.r. spectrum, with its single Me_3Ge resonance, is compatible with this interpretation if these two isomers are interconverting rapidly on the n.m.r. time scale. Cooling a solution of (VI) to −100° caused no change in the n.m.r. spectrum, however, so that the activation energy for any such process must be small. It would not be unreasonable to encounter this phenomenon here, since intramolecular dynamic *cis–trans*-isomerism has been observed for the related $[Os(CO)_4(MMe_3)_2]$ (M = Si or Sn) species.[14]

On heating a pure sample of (VI) in heptane, compounds (III; M = Ge) and (IV) were formed, showing that (VI) is a precursor of the tetrahydropentalenyl complexes. In 42 h, total conversion into these and into $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ occurs. Neither (III; M = Ge) nor (IV) is affected by heating in heptane. These data do not firmly establish that (VI) is an intermediate in the ring contraction reaction of cdt with (I; M = Ge).

---

[7] S. F. Watkins, *J. Chem. Soc.* (*A*), 1969, 1552.

[8] M. M. Crozat and S. F. Watkins, *J.C.S. Dalton*, 1972, 2512.

[9] P. Heimbach, P. W. Jolly, and H. Wilke, *Adv. Organometallic Chem.*, 1970, **8**, 50.

[10] T. H. Coffield, K. G. Ihrman, and W. Burns, *J. Amer. Chem. Soc.*, 1960, **82**, 4209.

[11] K. K. Joshi, R. H. B. Mais, F. Nyman, P. G. Owston, and A. M. Wood, *J. Chem. Soc.* (*A*), 1968, 318.

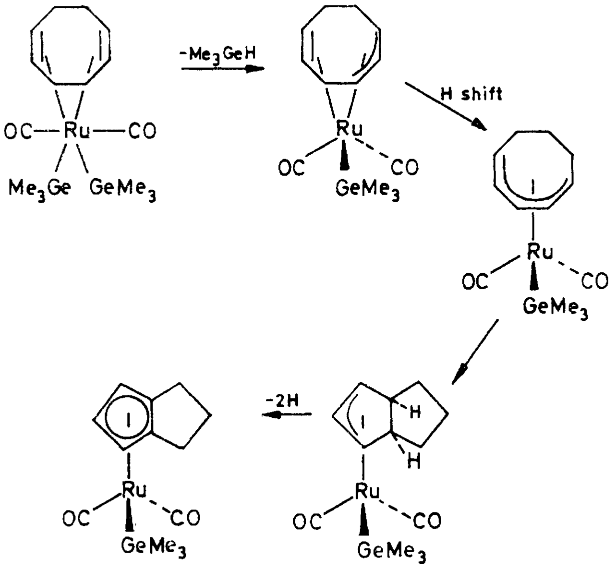
[12] H. Lehmkuhl, W. Leuchte, and E. Janssen, *J. Organometallic Chem.*, 1971, **30**, 407.

[13] S. Otsuka and T. Taketomi, *J.C.S. Dalton*, 1972, 1879.

[14] R. K. Pomeroy and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1972, **94**, 274.

Nevertheless, it seems likely that a transitory π-complex is formed initially, and this releases a C_4 fragment giving the bicyclo[3.3.0]hydrocarbon complexes observed, either directly or *via* (VI) or a π-complex related to it.

It is difficult to envisage a process by which the binuclear ruthenium complex (IV) is formed. Neither heating $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ with cod, nor heating (I; M = Ge) with (III; M = Ge) provided any trace of (IV).



SCHEME

A possible reaction sequence for the conversion of (VI) into (III; M = Ge), encompassing the proposals of Otsuka and Taketomi[13] for a similar cobalt-assisted ring closure, is outlined in the Scheme. However, the 1,2,3,5,6-η-octadienyl complex and/or the 1-5-η-octadienyl complex postulated as intermediates might be expected to have been isolable. This expectation is reinforced by the recent report of the isolation of the tricarbonylmanganese analogues (VII) and (VIII) from the reaction of cyclo-octa-1,3,5-triene and $[Mn_3H_3(CO)_{12}]$.[15]

Undoubtedly the tendency for the $Ru(CO)_2(GeMe_3)$ system to bond strongly with the cyclopentadienyl group provides a driving force for formation of the tetrahydropentalenyl ligand in these reactions with cod or cdt. The degradation of norbornadiene by the cobalt–acetylene complexes $[Co_2(CO)_6(RC_2R')]$ to afford $[Co(CO)_2(\pi\text{-}C_5H_5)]$ is another manifestation of this phenomenon, a C_2 fragment being lost in this case.[16]

Cyclododecatriene also undergoes ring contraction on reaction with (I; M = Si), but to give only low yields of (III; M = Si) and the fluxional complex $[Ru_2(CO)_6(C_8H_{10})]$, (IX). This latter complex, the iron analogue of which is known,[17] is readily prepared by treating $Ru_3(CO)_{12}$ or various organo-(Group IVB)-(carbonyl)-ruthenium species with cyclo-octa-1,3,5-triene; its chemistry is described in detail in the following paper.[18]

The complexes (III; M = Si) and $[Ru_2(CO)_6(C_8H_{10})]$ are also formed, again in low yield, on treatment of (II; M = Si) with cod or cdt. With the latter, however, the major product (60%) is $[Ru_3(CO)_9(C_{12}H_{15})H]$.[19] Compound (II; M = Ge), on the other hand, reacts with both cdt and cod to afford $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ and $[Ru(CO)_3(\mu\text{-}GeMe_2)]_3$[4b] as the major products. With cyclo-octa-1,5-diene, compounds (III; M = Ge) and (IV) are also formed, while with cdt a yellow crystalline complex is produced (*ca.* 20% yield), which has so far eluded identification. The mass spectrum indicates a molecular ion with an isotope distribution compatible with an Ru_3Ge heavy-atom framework. Only very broad weak signals are discernible in the ^1H n.m.r. spectrum and, although this would be unusual for complexes of this general type, the compound may be a paramagnetic species.

In the absence of solvent, in sealed tubes at 150°, cod and (II; M = Si) react with release of trimethylsilane and formation in low yield of (III; M = Si), $Ru_2(CO)_6(C_8H_{10})$, the known[20] cyclo-octa-1,5-diene complex $[Ru(CO)_3(C_8H_{12})]$, $Ru_3(CO)_{12}$, and a small amount of a complex $[Ru_4(CO)_{12}(C_8H_{10})]$ obtained previously[21] from cod and $[Ru_4(CO)_{12}H_4]$. A sealed-tube reaction of cod and (II; M = Ge) also give a cluster complex with a mass spectrum $[(M - n\text{CO})^+;\ n = 0\text{—}12]$ in accord with the same formulation, $[Ru_4(CO)_{12}(C_8H_{10})]$, but the i.r. spectrum (ν_{CO} 2069s, 2060s, 2046m, 2019w, 2006m, 2001w, 1978w, and 1895w cm^{-1}) indicates the presence of a (probably asymmetric) bridging CO group, unlike the structure of the known $[Ru_4(CO)_{12}(C_8H_{10})]$. The structures of both our products are probably related to that of $[Ru_4(CO)_{11}(C_8H_{10})]$.[22]

A rearrangement of the relative orientation of the trimethylgermyl ligands in (VI) takes place on displacement of the cod ligand by trimethyl phosphite. The product, $[Ru(GeMe_3)_2(CO)_2\{P(OMe)_3\}_2]$, has an all-*trans*-configuration; it shows one strong carbonyl absorption in the i.r., and one Me_3Ge n.m.r. signal. Strong phosphorus–phosphorus coupling revealed in a virtual triplet for the methoxy-protons is diagnostic of a *trans* arrangement of the $P(OMe)_3$ ligands.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on a Varian HA100 spectrometer and mass spectra with A.E.I. MS 902 and

---

[15] R. B. King and M. N. Ackermann, Abstracts of the VIth Internat. Conf. Organometallic Chem., Amherst, U.S.A., 1973, paper 72.

[16] I. U. Khand, G. R. Knox, P. L. Pauson, W. E. Watts, and M. I. Foreman, *J.C.S. Perkin I*, 1973, 977.

[17] F. A. Cotton and T. J. Marks, *J. Organometallic Chem.*, 1969, **19**, 237.

[18] A. C. Szary, S. A. R. Knox, and F. G. A. Stone, following paper.

[19] M. I. Bruce, M. A. Cairns, and M. Green, *J.C.S. Dalton*, 1972, 1293.

[20] F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624.

[21] A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 2056.

[22] R. Mason and K. M. Thomas, *J. Organometallic Chem.*, 1972, **3**, C39.

MS 30 instruments operating at 70 eV. Hydrocarbon solvents were purified by stirring with concentrated sulphuric acid and dried by distillation from calcium hydride. All reactions were performed under nitrogen or in sealed evacuated Pyrex tubes. Chromatography was carried out on silica gel columns, with hexane as eluant.

Reactions of all-trans-*Cyclododeca*-1,5,9-*triene*.—(a) *With* $[Ru(CO)_4(GeMe_3)_2]$ (I; M = Ge). (i) A solution of (I; M = Ge) (750 mg, 1·66 mmol) and cdt (800 mg, 4·9 mmol) was heated in heptane at reflux (97°) for 59 h. The solvent was removed and the residue was chromatographed, giving in order of elution, $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ (60 mg, 9%), identified by its i.r. spectrum;[4b] $[Ru(CO)_2(GeMe_3)(C_8H_9)]$ (III; M = Ge) as a yellow *liquid* (72 mg, 11%) (Found: C, 40·8; H, 4·7%; *M*, 380. $C_{13}H_{18}GeO_2Ru$ requires C, 39·6; H, 5·1%; *M*, 380), purified by distillation (50—70° at 10^{-2} mmHg) onto a water-cooled probe; yellow *crystals* of $[Ru_2(CO)_4(GeMe_3)(\mu\text{-}GeMe_2)_2(C_8H_9)]$ (IV) (29 mg, 5%) (Found: C, 30·6; H, 4·0; Ru + Ge, 56·8%; *M*, 744. $C_{19}H_{30}Ge_3O_4Ru_2$ requires C, 30·3; H, 4·0; Ru + Ge, 56·5%; *M*, 744); and (V) (53 mg, 10%), identified by i.r. and mass spectra.[6]

(ii) A sealed tube containing (I; M = Ge) (200 mg, 0·44 mmol) and cdt (200 mg, 1·23 mmol) was heated at 150° for 3 days, then volatile products were taken through traps held at −78 and −196°. A small amount of Me_3GeH, identified by i.r., condensed in the latter. Chromatography of the orange involatile residue yielded only $[Ru(CO)_3(\mu\text{-}GeMe_2)]_3$ (52 mg, 41%), identified by i.r. spectroscopy.

(b) *With* $[Ru(CO)_4(GeMe_3)]_2$ (II; M = Ge). A solution of (II; M = Ge) (170 mg, 0·24 mmol) and cdt (200 mg, 1·23 mmol) in heptane was heated at reflux for 14 h. Removal of solvent and chromatography gave $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ (20 mg, 10%) and $[Ru(CO)_3(\mu\text{-}GeMe_2)]_3$ (61 mg, 42%), identified by i.r. spectroscopy,[4b] and unidentified yellow crystals (30 mg) (ν_{CO} 2078w, 2038w, 2006s, and 1999vs cm^{-1}; *M*, 854).

(c) *With* $[Ru(CO)_4(SiMe_3)_2]$ (I; M = Si). A solution of (I; M = Si) (210 mg, 0·58 mmol) and cdt (500 mg, 3·1 mmol) in heptane was heated at reflux for 48 h. Chromatography then gave small amounts of both $[Ru(CO)_2(GeMe_3)(C_8H_9)]$ (III; M = Si), identified by mass (Found: *M*, 336. $C_{13}H_{18}O_2RuSi$ requires *M*, 336), i.r., and n.m.r. spectra, purified by distillation (65° and 10^{-2} mmHg) onto a water-cooled probe, and $[Ru_2(CO)_6(C_8H_{10})]$, identified by i.r. spectroscopy.[18]

(d) *With* $[Ru(CO)_4(SiMe_3)]_2$ (II; M = Si). After heating (7 h) a solution of (II; M = Si) (250 mg, 0·44 mmol) and cdt (300 mg, 1·9 mmol) in heptane, chromatography gave yellow crystalline $[Ru_3(CO)_9(C_{12}H_{15})H]$[19] (126 mg, 62%) and small amounts of (III; M = Si) and $[Ru_2(CO)_6(C_8H_{10})]$, identified by i.r. spectroscopy.[18]

Reactions of Cyclo-octa-1,5-*diene*.—(a) *With* $[Ru(CO)_4(GeMe_3)_2]$ (I; M = Ge). (i) Heating (I; M = Ge) (500 mg, 1·11 mmol) in heptane (42 h) with cod (550 mg, 5·1 mmol), followed by chromatography, gave, in order of elution, colourless *crystals* of $[Ru(CO)_2(GeMe_3)_2(C_8H_{12})]$ (VI) (182 mg, 33%) (Found: C, 38·2; H, 6·0; Ru + Ge, 49·4%; *M*, 502. $C_{16}H_{30}Ge_2O_2Ru$ requires C, 38·2; H, 5·9; Ru + Ge, 49·6%; *M*, 502), purified by sublimation (25° and 10^{-2} mmHg), and $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ (36 mg, 8%), (III; M = Ge) (95 mg, 23%), and (IV) (52 mg, 13%), identified by i.r. spectroscopy.

(ii) Heating (150°; 3 days) an evacuated sealed tube containing (I; M = Ge) (200 mg, 0·44 mmol) and cod (330 mg, 3·1 mmol), followed by chromatography, gave only spectroscopically identified[4b] $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ (58 mg, 33%) and $[Ru(CO)_3(\mu\text{-}GeMe_2)]_3$ (52 mg, 41%) as products in other than trace amounts.

(b) *With* $[Ru(CO)_4(GeMe_3)]_2$ (II; M = Ge). (i) Heating (15 h) (II; M = Ge) (100 mg, 0·15 mmol) and cod (220 mg, 2·0 mmol) in heptane at reflux, followed by chromatography, gave $[Ru(CO)_3(\mu\text{-}GeMe_2)]_3$ (28 mg, 32%), (III; M = Ge) (28 mg, 25%), and (IV) (18 mg, 16%), all identified by i.r. spectroscopy.

(ii) Heating (150°; 2 days) a sealed tube containing (II; M = Ge) (250 mg; 0·38 mmol) and cod (330 mg, 3·1 mmol) gave a deep purple mixture, which on chromatography afforded the known[20] $[Ru(CO)_3(C_8H_{12})]$ (18 mg, 8%), $[Ru(CO)_3(\mu\text{-}GeMe_2)]_3$ (90 mg, 42%), and $[Ru_2(CO)_6(C_8H_{10})]$ (7 mg, 4%), all identified by their i.r. and mass spectra, as well as purple *crystalline* $[Ru_4(CO)_{12}(C_8H_{10})]$ (16 mg, 10%) (Found: *M*, 848. $C_{16}H_{10}O_8Ru_4$ requires *M*, 848), ν_{CO} 2069s, 2060s, 2046m, 2019w, 2006m, 2001w, 1978w, and 1895w cm^{-1}; and the known[21] purple $[Ru_4(CO)_{12}(C_8H_{10})]$ (15 mg, 10%) (Found: *M*, 848. $C_{16}H_{10}O_8Ru_4$ requires *M*, 848).

(c) *With* $[Ru(CO)_4(SiMe_3)_2]$ (I; M = Si). Heating (15 h) a heptane solution of (I; M = Si) (200 mg, 0·56 mmol) and cod (620 mg, 5·7 mmol), followed by chromatography, gave $[Ru_2(CO)_6(C_8H_{10})]$ (13 mg, 10%) and (III; M = Si) (34 mg, 18%), identified by i.r. spectroscopy.

(d) *With* $[Ru(CO)_4(SiMe_3)]_2$ (II; M = Si). (i) After heating (14 h) a mixture of (II; M = Si) (200 mg, 0·35 mmol) and cod (220 mg, 2·0 mmol) in heptane, chromatography gave $[Ru_2(CO)_6(C_8H_{10})]$ (10 mg, 6%) and (III; M = Si) (44 mg, 19%), identified by i.r. spectroscopy.

(ii) Heating (150°; 28 h) a sealed tube containing (II; M = Si) (100 mg, 0·17 mmol) and cod (400 mg, 3·7 mmol) gave a purple mixture. Fractionation of volatile material gave a small amount of Me_3SiH (−196° trap), identified by its i.r. spectrum. Chromatography of the residue yielded $[Ru(CO)_3(C_8H_{12})]$[20] (11 mg, 11%), $[Ru_2(CO)_6(C_8H_{10})]$ (7 mg, 9%), (III; M = Si) (16 mg, 14%), and $Ru_3(CO)_{12}$ (16 mg, 22%) on elution with hexane (all identified by i.r. spectroscopy). Dichloromethane–hexane (3 : 7) then eluted the known $[Ru_4(CO)_{12}(C_8H_{10})]$ (10 mg, 4%), identified by i.r. and mass spectra.

Reactions of $Ru(CO)_2(GeMe_3)_2(C_8H_{12})$ (VI).—(a) *Action of heat*. Heating a solution of (VI) (50 mg, 0·1 mmol) under reflux for 42 h, followed by chromatography, gave $[Ru(CO)_3(GeMe_3)(\mu\text{-}GeMe_2)]_2$ (8 mg, 20%), (III; M = Ge) (16 mg, 42%), and (IV) (13 mg, 35%), identified by i.r. spectroscopy.

(b) *With* $P(OMe)_3$. Heating (VI) (150 mg, 0·3 mmol) with $P(OMe)_3$ (250 mg, 2·0 mmol) in hexane for 8 h, followed by chromatography (elution with 1 : 4 dichloromethane–hexane), gave colourless *crystals* of *all*-*trans*-$[Ru(CO)_2(GeMe_3)_2\{P(OMe)_3\}_2]$ (175 mg, 91%) (Found: C, 29·0; H, 6·2%; *M*, 642. $C_{14}H_{36}Ge_2O_8P_2Ru$ requires C, 29·7; H, 6·2%; *M*, 642).

We thank the S.R.C. for a research studentship (to R. P. P.) and the U.S.A.F. Office of Scientific Research for support.

[3/2129 *Received*, 18*th October*, 1973]