Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part IX.[1] Cycloheptadienyl- and Cycloheptatrienyl-carbonylosmium Complexes

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Treatment of the compounds $[Os(MR_3)_2(CO)_4]$ (MR_3 = $SiMe_3$, $SiMe_2Ph$, or $GeMe_3$) or $[\{Os(MR_3)(CO)_4\}_2]$ (MR_3 = $SiMe_3$ or $SiEt_3$) with cycloheptatriene or cyclohepta-1,3-diene yields cycloheptadienyl complexes $[Os(MR_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ as major products, and bridging cycloheptatrienyl complexes $[Os_2(MR_3)(CO)_5\text{-}(1—2,3—4\text{-}\eta : 5—7\text{-}\eta\text{-}C_7H_7)]$. In their i.r. spectra the cycloheptadienyl complexes exhibit three carbonyl stretching bands; and temperature-dependent ^1H n.m.r. spectra, attributed to restricted rotation about the osmium–cycloheptadienyl bond, allowing the existence of conformational isomers which interconvert rapidly at ambient temperature, but are observable on the n.m.r. time scale at low temperatures. Some reactions of the complex $[Os(SiMe_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ have been studied.

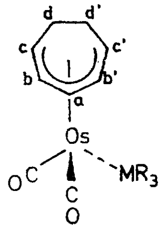
EARLIER [1], an investigation of the reactions of cyclooctatetraene with the carbonylosmium complexes $[Os(MMe_3)_2(CO)_4]$ (M = Si or Ge) and $[\{Os(SiMe_3)(CO)_4\}_2]$ was described. Unlike reactions with the corresponding carbonylruthenium complexes,[2] no species containing pentalene stabilised by co-ordination to a metal were observed, and this was related to a possibly reduced tendency of the MMe_3 ligand to migrate from osmium to a co-ordinated hydrocarbon. Previous studies [2] had shown that such a migration was a vital step in pentalene complex formation from $[Ru(MMe_3)_2(CO)_4]$ and cyclooctatetraene. Migration of MMe_3 ligands from ruthenium occurs readily on reaction of the complexes $[Ru(MMe_3)_2(CO)_4]$ (M = Si or Ge) with cycloheptatriene (cht), forming the substituted cycloheptadienyl complexes $[Ru(MMe_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_8MMe_3\text{-}6)]$ in high yield.[3] Treatment of $[Os(MR_3)_2(CO)_4]$ with cht would therefore provide a good test of the capability of MR_3 ligands to migrate from osmium to a C_n-ring and it is these reactions, and also those of $[\{Os(MR_3)(CO)_4\}_2]$ with cht, which we describe here.

RESULTS AND DISCUSSION

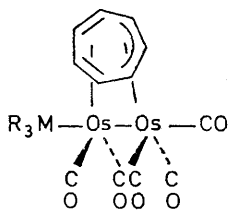
Both $[Os(MR_3)_2(CO)_4]$ (MR_3 = $SiMe_3$, $SiMe_2Ph$, or $GeMe_3$) and $[\{Os(MR_3)(CO)_4\}_2]$ (MR_3 = $SiMe_3$ or $SiEt_3$) react with cht less readily than their ruthenium analogues, but at a convenient rate in octane under reflux (completion after 3 to 4 days). The major product in each case is a colourless, low-melting, crystalline cycloheptadienyl complex $[Os(MR_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ (1), with a low yield of the corresponding yellow crystalline cycloheptatrienyl complex $[Os_2(MR_3)(CO)_5(1—2,3—4\text{-}\eta : 5—7\text{-}\eta\text{-}C_7H_7)]$ (2) for all but MR_3 = $SiEt_3$. We were not able to prepare $[Os(SiEt_3)_2(CO)_4]$, but $[OsH(SiEt_3)(CO)_4]$ likewise gave only $[Os(SiEt_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ with cht. Neither $[\{Os(SiPh_3)(CO)_4\}_2]$ nor $[\{Os(SiMeCl_2)(CO)_4\}_2]$ gave either type of complex with cht; no products were isolated following reaction with the latter, and only $[H_4Os_4(CO)_{12}]$ and $[Os_3(CO)_{12}]$ from the former. Similar results are obtained when the $[Os(MR_3)_2(CO)_4]$ and $[\{Os(MR_3)(CO)_4\}_2]$ complexes are treated with cyclohepta-1,3-diene, save that a low yield (*ca.* 10%) of $[Os(CO)_3(1—4\text{-}\eta\text{-}C_7H_{10})]$ is produced at the expense of a decrease in yield of the other products.

No evidence was obtained for formation in these reactions of any species resulting from MR_3 group migration to the C_7-ring. Thus although an MR_3 group is lost from osmium, hydrogen abstraction (presumably from the solvent) by cht is evidently more favourable than MR_3 migration as a means of generating a cycloheptadienyl ligand. This parallels the observation [1] that 1,2,3,3a,6a-η-1,4,5,6-tetrahydropentalenyl complexes $[Os(MMe_3)(CO)_2(C_8H_9)]$ (M = Si or Ge) are preferentially formed on reaction of $[Os(MMe_3)_2(CO)_4]$ with cyclo-octatetraene, and allows the conclusion that MR_3 ligand migrations are of little or no importance in reactions of the osmium complexes $[Os(MR_3)_2(CO)_4]$ and $[\{Os(MR_3)(CO)_4\}_2]$.

The properties (Table 1) of the complexes $[Os_2(MR_3)(CO)_5(1—2,3—4\text{-}\eta : 5—7\text{-}\eta\text{-}C_7H_7)]$ are compatible with their formulation as the osmium analogues (2) of the known[3,4] bridging cyclo-heptatrienyl species $[Ru_2(MMe_3)(CO)_5(1—2,3—4\text{-}\eta : 5—7\text{-}\eta\text{-}C_7H_7)]$ (M = Si or Ge). Like the latter, complexes (2) are fluxional, showing a singlet signal in their ^1H n.m.r. spectra for the cycloheptatrienyl ring protons both at room temperature and at −100 °C. Their mass spectra show parent ions with an isotope distribution pattern as expected for an Os_2Si species. Loss of five carbonyl groups from the molecular ions is readily observable.



(1)



(2)

The complexes (1) have spectroscopic properties of considerably more interest than their ruthenium analogues.[5] Although elemental analyses are in accord with the dicarbonyl formulation (1), and mass spectra (at both 12 and 70 eV) show no ions heavier than those corresponding to $[Os(MR_3)(CO)_2(C_7H_9)]^+$, their i.r. spectra

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[1] Part VIII. P. J. Harris, J. A. K. Howard, S. A. R. Knox, R. P. Phillips, F. G. A. Stone, and P. Woodward, *J.C.S. Dalton*, 1976, 377.

[2] S. A. R. Knox and F. G. A. Stone, *Accounts Chem. Res.*, 1974, 7, 321.

[3] A. Brookes, S. A. R. Knox, V. Riera, B. A. Sosinsky, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 1641.

[4] J. A. K. Howard and P. Woodward, *J.C.S. Dalton*, 1975, 59.

[5] B. A. Sosinsky, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 1633.

have *three* strong carbonyl stretching bands, the band at lowest frequency being of highest intensity. Repeated crystallisation, sublimation, and chromatography of the complexes did not alter their i.r. spectra, the band pattern of which is quite untypical of a tricarbonylmetal grouping. In view of the data, it seemed apparent that the complexes (1) existed as an isomeric mixture of two *di*-carbonylosmium species. The observed spectra are compatible with this interpretation provided that the two isomers have slightly differing separations of their two carbonyl bands, and that the lower-energy bands of each species are accidentally degenerate.

TABLE 1

I.r. and ^{1}H n.m.r. data for the osmium complexes

Complex	ν_{CO}/cm^{-1} [a]	Chemical shift (τ) [b]
$[Os(SiMe_2Ph)_2(CO)_4]$	2 014s	2.63 (10 H, m), 9.13 (12 H, s)
$[\{Os(SiMeCl_2)(CO)_4\}_2]$	2 095w, 2 082w, 2 058s	8.68s
$[Os(SiMe_3)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	2 015s, 2 009s, 1 955s	4.11 (1 H, t), 4.80 (2 H, dd), 5.88 (2 H, m), 8.00 (4 H, m), 9.65 (9 H, s)
$[Os(SiEt_3)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	2 015s, 2 010s, 1 957s	4.23 (1 H, t), 4.80 (2 H, dd), 5.75 (2 H, m) 8.05 (4 H, m), 9.15 (15 H, t)
$[Os(SiMe_2Ph)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	2 015s, 2 009s, 1 955s	2.60 (5 H, m), 4.40 (1 H, t), 4.93 (2 H, dd), 6.03 (2 H, m), 8.17 (4 H, m), 9.40 (6 H, s)
$[Os(GeMe_3)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	2 015s, 2 010s, 1 961s	4.03 (1 H, t), 4.82 (2 H, dd), 5.93 (2 H, m), 8.06 (4 H, m), 9.55 (9 H, s)
$[OsBr(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	2 048s, 1 999s, 1 994sh	3.31 (1 H, t), 4.24 (2 H, dd), 5.52 (2 H, m), 7.88 (4 H, m)
$[OsI(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	2 044s, 1 997s, 1 992sh	3.42 (1 H, t), 4.15 (2 H, dd), 5.50 (2 H, m), 7.94 (4 H, m)
$[Os_2(SiMe_3)(CO)_5(1\text{—}2,3\text{—}4\text{-}\eta : 5\text{—}7\text{-}\eta\text{-}C_7H_7)]$	2 065s, 2 002s, 1 997s, 1 975m, 1 948m	6.29 (7 H, s), 9.65 (9 H, s)
$[Os_2(SiMe_2Ph)(CO)_5(1\text{—}2,3\text{—}4\text{-}\eta : 5\text{—}7\text{-}\eta\text{-}C_7H_7)]$	2 068s, 2 005s, 1 999s, 1 977m, 1 949m	2.54 (5 H, m), 6.28 (7 H, s), 9.26 (6 H, s)
$[Os_2(GeMe_3)(CO)_5(1\text{—}2,3\text{—}4\text{-}\eta : 5\text{—}7\text{-}\eta\text{-}C_7H_7)]$	2 061s, 2 001s, 1 994s, 1 971m, 1 946m	6.24 (7 H, s), 9.43 (9 H, s)
$[Os(CO)_3(1\text{—}4\text{-}\eta\text{-}C_7H_{10})]$	2 063s, 1 987s, 1 981s	4.61 (2 H, dd), 6.89 (2 H, m), 8.19 (4 H, m), 8.62 (2 H, m)
$[Os(CO)\{P(OMe)_3\}_2(1\text{—}5\text{-}\eta\text{-}C_7H_7)]I$	1 977s [c]	6.16 (7 H, s), 6.18 (9 H, d, *J* 16), 6.28 (9 H, d, *J* 16)

[a] In cyclohexane. [b] $CDCl_3$ solution. [c] CCl_4 solution.

TABLE 2

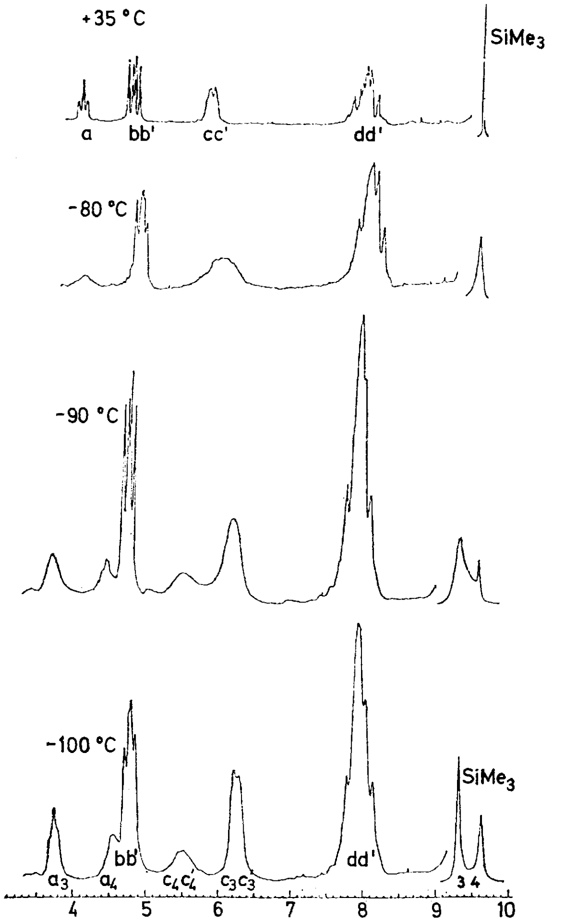
Analytical and physical data for the osmium complexes [a]

				Analyses (%)		
Compound	Colour	M.p. (*t*/°C)	Yield (%)	C	H	*M* [b]
$[Os(SiMe_2Ph)_2(CO)_4]$	Pale yellow	92—94	75	42.3 (41.8)	4.0 (3.8)	574 (574)
$[\{Os(SiMeCl_2)(CO)_4\}_2]$ [c]	Colourless	120 (dec.)	90	14.0 (14.4)	1.1 (0.7)	776 (776)
$[Os(SiMe_3)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ [d]	Colourless	44—45	82	35.2 (34.8)	4.5 (4.4)	414 (414)
$[Os(SiEt_3)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	Colourless	26—27	90	39.7 (39.5)	5.3 (5.3)	456 (456)
$[Os(SiMe_2Ph)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	Colourless	37—38	71	42.9 (42.9)	4.2 (4.2)	476 (476)
$[Os(GeMe_3)(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	Colourless	48	53	32.0 (31.4)	4.0 (3.9)	460 (460)
$[OsBr(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ [e]	Pale yellow	114 (dec.)	78	26.0 (25.7)	2.5 (2.1)	421 (421)
$[OsI(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	Yellow	122—124	83	23.4 (23.1)	2.0 (1.9)	542 (542)
$[Os_2(SiMe_3)(CO)_5(1\text{—}2,3\text{—}4\text{-}\eta : 5\text{—}7\text{-}\eta\text{-}C_7H_7)]$	Yellow	176—177	8	26.6 (26.2)	2.5 (2.3)	686 (686)
$[Os_2(SiMe_2Ph)(CO)_5(1\text{—}2,3\text{—}4\text{-}\eta : 5\text{—}7\text{-}\eta\text{-}C_7H_7)]$	Yellow	163—164	14	32.2 (32.1)	2.6 (2.4)	748 (748)
$[Os_2(GeMe_3)(CO)_5(1\text{—}2,3\text{—}4\text{-}\eta : 5\text{—}7\text{-}\eta\text{-}C_7H_7)]$	Yellow	184 (dec.)	8	24.7 (24.6)	2.2 (2.2)	732 (732)
$[Os(CO)_3(1\text{—}4\text{-}\eta\text{-}C_7H_{10})]$	Colourless	50 [f]	10	32.5 (32.4)	2.7 (2.7)	370 (370)
$[Os(CO)\{P(OMe)_3\}_2(1\text{—}5\text{-}\eta\text{-}C_7H_7)]I$	Colourless	>250 (dec.)	82	23.1 (24.5)	3.4 (3.6)	

[a] Calculated values given in parentheses. [b] Mass spectrometry. [c] Found: Cl, 16.6. Reqd.: 16.8%. [d] Found: Os, 47.0; Si, 7.5. Reqd.: Os, 46.4; Si, 6.8%. [e] Found: Br, 18.7. Reqd.: 19.0%. [f] B.p. (10^{-2} mmHg).

The ^{1}H n.m.r. spectra of the complexes strongly support this interpretation in revealing the existence of interconverting conformational isomers (rotamers) which can be accounted for by restricted rotation about the osmium–cycloheptadienyl bond. The n.m.r. spectrum of (1; $MR_3 = SiMe_3$) at various temperatures is presented in the Figure; the spectra of (1; $MR_3 = SiEt_3$, $SiMe_2Ph$, or $GeMe_3$) are analogous, both in terms of their general form, and the temperatures at which the changes occur. It is apparent that the ambient temperature spectrum, which shows equivalence of the bb′ and cc′ pairs of protons, arises as a result of a rapid intramolecular averaging process. In other words, the isomers which are detected by i.r. spectroscopy are interconverting rapidly enough at this temperature to be unobserved on the slower time scale of n.m.r. spectroscopy. The barrier to their interconversion is high enough, however, for the lifetime of the isomers to be extended sufficiently at low temperature to allow their n.m.r. detection.

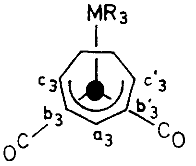
As the temperature is lowered, the signals due to the a and cc′ protons of the complexes (1) broaden on approaching −70 °C, and below −85 °C each separates into two signals of unequal intensity, limiting spectra being achieved at about −100 °C. For (1; $MR_3 = SiMe_3$, $SiMe_2Ph$, or $GeMe_3$) similar splitting is observed for the methyl protons, but for all the complexes (1) the double-doublet of the bb′ protons undergoes only slight broadening at the limit. These changes are at first sight consistent with the freezing out of two conformational isomers (3) and (4) each of which contains a plane of symmetry such that their bb′ and cc′ protons remain equivalent. We assign, for example, the −100 °C signals of (1; MR$_3$ = SiMe$_3$) at τ 3.89, 6.42, and 9.47, which are of relative intensity 1 : 2 : 9, to the a, cc′, and Me$_3$Si protons of one rotamer, and those at τ 4.69, 5.63, and 9.77, of the same 1 : 2 : 9 relative intensity, to the corresponding protons of the other rotamer. The bb′ and ring methylene protons (dd′) of each rotamer appear as signals of the correct intensity at τ 4.96 and 8.12 respectively; this assignment requires that the bb′ pair of protons, in addition to being equivalent within each rotamer, are of near identical chemical shift for both.



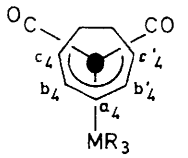
100 MHz ^{1}H n.m.r. spectrum of [Os(SiMe$_3$)(CO)$_2$(1—5-η-C$_7$H$_9$)] (1; MR$_3$ = SiMe$_3$) at various temperatures in CCl$_3$F solution

It might be anticipated, in view of the high[6] *trans*-effect of a trimethylsilyl group (higher than CO), that the a proton of isomer (3) would be strongly deshielded relative to that of (4), which has no ligand directly *trans* to itself. This being the case, the assignment of the lower field of the two a proton signals of (1; MR$_3$ = SiMe$_3$) to (3) is followed (on the basis of the signal intensities discussed above) by the assignment of the −100 °C spectrum as in the Figure. The more intense of the two Me$_3$Si signals will then be that corresponding to (3).

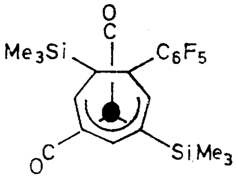
It is possible that the signals assigned to (4) arise as a result of a rapid interconversion of (5) and (6) through a very low-energy barrier. There is some evidence in the n.m.r. spectra of (1; MR$_3$ = SiMe$_3$ or GeMe$_3$) that such a situation exists, in that the signals attributed to (4) are broader at −100 °C [markedly for (1; MR$_3$ = GeMe$_3$)] than those assigned to (3), perhaps indicating the onset of a further freezing out of [5(6)]. The merit of this proposal is that the three conformational isomers which it introduces, two of which [(5) and (6)] are spectroscopically indistinguishable, all have the same basic orientation of ligands, an orientation which has been established in the solid state for the related [Ru(SiMe$_3$)(CO)$_2${1—5-η-C$_7$H$_7$(SiMe$_3$-6)(C$_6$F$_5$-7)}] (7) by *X*-ray diffraction.[7] Acceptance of the existence of (5) and (6) as an alternative to (4) does not alter the assignment of the n.m.r. spectra, for, although conformers are now being considered which have the a proton of the C$_7$H$_9$ ring directly *trans* to CO, the *trans*-effect of this ligand is (as previously mentioned) less than that of Me$_3$Si; the shifts of (3) are thus still assigned as before.



(3) ● = Os

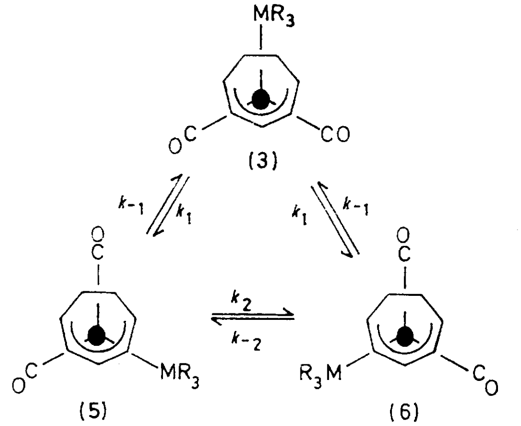


(4) ● = Os



(7) ● = Ru

The indicated Scheme (3) $\rightleftharpoons$ (5) $\rightleftharpoons$ (6) thus accounts equally well as does a (3) $\rightleftharpoons$ (4) interconversion for the observed i.r. and n.m.r. spectra of the complexes (1), with the proviso that the barriers to the k_1 and k_{-1} pathways are much larger than that of the k_2 pathway, so that a (5) $\rightleftharpoons$ (6) interconversion still proceeds rapidly at −100 °C. Obviously the attainment of lower temperatures would be required to establish whether the Scheme has any reality, but it is relevant that an identical Scheme



SCHEME

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

[7] J. A. K. Howard, S. A. R. Knox, V. Riera, B. A. Sosinsky, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1974, 673.

has been invoked to explain the variable-temperature ^{31}P n.m.r. spectra of the structurally related cycloheptadienyl complexes $[M(CO)_2(L)(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ (M = Mn or Re; L = 4-ethyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane).[8]

The populations of the conformational isomers (3) and (4) [it being understood that in this context (4) is interchangeable with (5) or (6)] vary substantially with the nature of the MR_3 group. The (3) : (4) ratio, which is given by the signal intensity ratio a_3/a_4 or $c_{33'}/c_{44'}$ {or in the case of (1; $MR_3 = SiMe_3$, $SiMe_2Ph$, or $GeMe_3$) by the methyl proton signals}, is 0.9 ± 0.1 for (1; $MR_3 = SiEt_3$ or $SiMe_2Ph$) but 2.0 ± 0.1 for (1; $MR_3 = SiMe_3$). This is consistent with a steric destabilisation of (3), which in having the MR_3 group adjacent to the methylene protons of the hydrocarbon ring, is likely to be more crowded than (4) [or (5) or (6)]. The predominance of (3) overall for (1; $MR_3 = SiMe_3$ and $GeMe_3$) [for which $(3)/(4) = 2.5 \pm 0.1$)], however, implies that in spite of steric preference for (4) [or (5) or (6)] other factors operate strongly in its favour. It seems probable, for example, that in (3) the carbonyl groups (taken together) experience less competition for osmium π-electron density from the cycloheptadienyl ligand than in the other conformers, which are thus disfavoured. Attempts to investigate more fully this obviously complex situation foundered on an inability (as described above) to prepare such complexes as (1; $MR_3 = SiPh_3$ and $SiMeCl_2$).

It is interesting to reconsider the i.r. spectra in the carbonyl region of the complexes (1) in the light of the information derived from their n.m.r. spectra. It is evident, on examination, that the relative intensities of the two high-frequency bands have a rough correlation with the relative stabilities of the rotamers. Thus (1; $MR_3 = GeMe_3$), for which rotamer (3) is predominant, has the higher-energy band of the two as the most intense, and it is this band which decreases in intensity through (1; $MR_3 = SiMe_3$) to (1; $MR_3 = SiEt_3$ or $SiMe_2Ph$) as rotamer (3) becomes progressively less stable relative to (4) [or (5) or (6)]. The assignment, therefore, of this band to the higher energy of the two bands of (3) seems reasonable.

The i.r. spectra of the halides $[OsX(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ (X = Br or I) (see below) show a basic two-band carbonyl pattern, but the lower-energy band has an unusually strong shoulder suggesting that these species also may exist as a mixture of rotamers. The n.m.r. spectra of the halides even at −100 °C, however, are similar to the room-temperature spectra of the complexes (1), so that rotation about the osmium–cycloheptadienyl bond must be relatively free. An equal freedom of rotation is evident for the ruthenium analogues[5] of (1), which exhibit a simple two-band carbonyl i.r. spectrum, and an averaged ^1H n.m.r. spectrum between room temperature and −100 °C. Since steric interactions between the ligand $1\text{—}5\text{-}\eta\text{-}C_7H_9$ and the other substituents on the metal would be greater for ruthenium than for osmium, this suggests that these restricted rotation phenomena are mainly electronic in origin.

Restricted rotation about a metal–cycloheptadienyl linkage has now been observed in several systems. Although Otsuka and Taketomi[9] originally attributed the variable-temperature ^1H n.m.r. spectrum of the cyclo-octa-1,5-diene complex $[Co(1,2,5,6\text{-}\eta\text{-}C_8H_{12})(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ in terms of a rotation of the cyclo-octadiene, Federov[10] has more recently suggested that a rotation of the cycloheptadienyl ligand is more likely. This latter explanation is supported by the n.m.r. spectrum of $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)_2]$, which clearly reveals the consequences of a restricted internal rotation about the metal–cycloheptadienyl bond.[11] Whitesides, in addition to his work[8] on $[M(CO)_2(L)(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ complexes mentioned earlier, has also reported[12] the observation by low-temperature n.m.r. of a cycloheptadienyl ring oscillation in the cluster complex $[Ru_3(CO)_6(1\text{—}5\text{-}\eta\text{-}C_7H_9)(1\text{—}7\text{-}\eta\text{-}C_7H_7)]$.

Compound (1; $MR_3 = SiMe_3$) reacts readily with bromine or iodine to give the halogeno-complexes $[OsX(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ (X = Br or I). The ruthenium analogues have been prepared[13] by halogen cleavage of the cluster complex $[Ru_3(CO)_6(1\text{—}5\text{-}\eta\text{-}C_7H_9)(1\text{—}7\text{-}\eta\text{-}C_7H_7)]$. Reaction of the complex $[OsI(CO)_2(\eta^5\text{-}C_7H_9)]$ with methyl-lithium led to extensive decomposition, and no methylosmium compound was isolated. The iodo-compound reacted with trimethyl phosphite in an unusual manner, since the product is best formulated as the salt $[Os(CO)\{P(OMe)_3\}_2(1\text{—}5\text{-}\eta\text{-}C_7H_7)]I$. In the i.r. region one ν_{CO} stretch was observed, and the proton n.m.r. spectrum indicated the presence of a fluxional C_7H_7-ring, signals due to CH_2 groups being absent. Two OCH_3 signals were observed as doublets ($J_{PH} = 16$ Hz) suggesting a *cis*-arrangement of the $P(OMe)_3$ ligands. The presence of I^- could be detected by silver nitrate, and the compound decomposed above 250 °C. It is suggested that one of the double bonds in the C_7H_7 ligand is not co-ordinated to osmium, but formation of this ligand by loss of hydrogen from C_7H_9 in this reaction is surprising.

The reaction between $[OsBr(CO)_2(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$ and the anion $[Re(CO)_5]^-$ proceeds readily in tetrahydrofuran. Chromatography of the ensuing mixture afforded a substantial amount of decacarbonyldirhenium and a very low yield of a complex of probable formulation $[(OC)_5Re\text{–}Os(CO)_2(C_7H_9)]$. The i.r. spectrum in the carbonyl stretching region was complex (2 094m, 1 997s, 1 990vs, 1 964s, and 1 941m cm^{-1}), the three bands at highest wavenumber having a pattern characteristic of an $(OC)_5M$ group. The mass spectrum showed a peak at *m/e* 666 corresponding to a molecular ion, followed by peaks due to the loss of seven CO groups. A strong peak at *m/e* 341 corresponded to $[Os(CO)_2(C_7H_9)]^+$.

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EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 257 instrument, and ^1H n.m.r. spectra with Varian Associates T60 and HA100 spectrometers. Mass spectra were determined with A.E.I. MS902 and MS30 instruments operating at 12 and 70 eV*. All hydrocarbon solvents were purified by stirring with concentrated sulphuric acid, and dried by distillation from calcium hydride. Chromatography was carried out on Florisil-packed columns using hexane as eluant. Spectroscopic data are summarised in Table 1, and the analytical data in Table 2.

The compounds $[Os(MR_3)_2(CO)_4]$ ($MR_3 = SiMe_3$ or $GeMe_3$), $[OsH(SiEt_3)(CO)_4]$, and $[\{Os(MR_3)(CO)_4\}_2]$ ($MR_3 = SiMe_3$ or $SiEt_3$) were prepared as described earlier.[14] The new compounds $[Os(SiMe_2Ph)_2(CO)_4]$ and $[\{Os(SiMeCl_2)(CO)_4\}_2]$ (Tables 1 and 2) were similarly prepared.

Reactions with Cycloheptatriene and Cyclohepta-1,5-*diene*.—In a typical experiment, $[Os(SiMe_3)_2(CO)_4]$ (850 mg, 1.89 mmol) and cycloheptatriene (1.5 g, 16.3 mmol) were heated under reflux in octane for 84 h. Removal of solvent *in vacuo* followed by chromatography in hexane of the residue afforded, in order of elution, colourless *crystals* of $[Os(SiMe_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ (642 mg, 82%) and yellow *crystals* of $[Os_2(SiMe_3)(CO)_5(1—2,3—4\text{-}\eta : 5—7\text{-}\eta\text{-}C_7H_7)]$ (52 mg, 8%). The former complex was purified by sublimation (30 °C/10^{-2} mmHg) followed by crystallisation from hexane at −78 °C The latter complex was purified by slow crystallisation from hexane at room temperature.

The other compounds (Table 2) containing $1—5\text{-}\eta\text{-}C_7H_9$ and $1—2,3—4\text{-}\eta : 5—7\text{-}\eta\text{-}C_7H_7$ ligands were similarly prepared.

Reactions of $[Os(SiMe_3)(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ *with Bromine and Iodine*.—A hexane solution of (1; $MR_3 = SiMe_3$) (300 mg, 0.72 mmol) was stirred at 0 °C whilst a solution of bromine (60 mg, 0.38 mmol) was added dropwise (1 h). Chromatography, eluting with a hexane–dichloromethane mixture (1 : 1), afforded pale yellow *crystals* of $[OsBr(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ (236 mg, 78%).

The iodo-complex (Table 2) was similarly prepared.

Formation of the Salt $[Os(CO)\{P(OMe)_3\}_2(C_7H_7)]I$.—Reaction between $[OsI(CO)_2(1—5\text{-}\eta\text{-}C_7H_9)]$ (40 mg, 0.09 mmol) and an excess of $P(OMe)_3$ (205 mg, 1.65 mmol) proceeded in hexane under reflux (48 h). When cooled to room temperature the mixture afforded colourless *crystals*, sparingly soluble in hydrocarbon solvents, formulated as $[Os(CO)\{P(OMe)_3\}_2(1—5\text{-}\eta\text{-}C_7H_7)]I$ (51 mg, 82%).

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* 1 eV ≈ 1.60×10^{-19} J.

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