Chemistry of the Metal Carbonyls. Part LXVI.[1] Complexes Derived from a Carbonylosmium Anion

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Reduction of dodecacarbonyltriosmium with sodium in liquid ammonia affords a cream solid which reacts with halides to afford complexes $Os(CO)_4X_2$ (X = Me, H_3Ge, Ph_3Sn, Me_3Pb, and $AuPPh_3$) in good yield, as well as lower yield formation of hydrido-species $Os(CO)_4(X)(H)$ (X = Me, H_3Ge, Me_3Sn). With dimethyltin dichloride the tin–osmium heterocycle $[Os(CO)_4SnMe_2]_2$ is formed, while protonation affords $Os(CO)_4H_2$.

THAT anions derived from transition-metal carbonyls are valuable in organometallic syntheses is well recognized.[2] Within the Fe, Ru, Os triad many carbonyl anions of iron are known, but relatively few of ruthenium or osmium. Of the carbonyliron anions, the tetracarbonylferrate(—II) ion has been most widely employed preparatively and is often prepared[3] as $Na_2Fe(CO)_4$ from dodecacarbonyltri-iron and sodium in liquid ammonia. Thus far only two reports[4,5] describing the utilisation of carbonylruthenium anions have appeared, both concerned with the material obtained by treating dodecacarbonyltriruthenium with sodium in liquid ammonia, and which is thought[4] to be either $NaHRu(CO)_4$ or a mixture of this compound with $Na_2Ru(CO)_4$. Recently some reactions of the tetracarbonyl(hydrido)osmium anion, $[Os(CO)_4H]^-$, have been described,[6] this species being obtained through the action of a sodium sand upon $Os(CO)_4H_2$. The investigation described here was undertaken with a view to establishing a convenient route to mononuclear carbonylosmium complexes *via* reaction of the readily available[7] dodecacarbonyltriosmium with sodium in liquid ammonia.

Like the dodecacarbonyls of iron and ruthenium, dodecacarbonyltriosmium is consumed rapidly by a solution of sodium in liquid ammonia, producing a cream solid on evaporation of solvent. Unlike the very air-sensitive materials obtained from the former two carbonyls, however, that generated from $Os_3(CO)_{12}$ is stable to air. The product differs from $NaHOs(CO)_4$, as prepared by L'Eplattenier,[6] in being only slightly soluble in tetrahydrofuran. Nevertheless, a saturated solution in this solvent does reveal carbonyl stretching absorptions (2042w, 2010s, 1935m, 1880vs, 1846s cm^{-1}) in the i.r. region, the latter four of which are attributable to $[Os(CO)_4H]^-$. I.r. (2083w, 2057m, 2025m, 2013m, 2000s, 1982m, 1940s,br, 1917w, cm^{-1}) and Raman (2058m, 1983s, 1915s, 1881m cm^{-1}) spectra of an easily formed aqueous solution of the reduction product exhibit absorptions which do not correspond to $NaHOs(CO)_4$ and are inconsistent with $Na_2Os(CO)_4$. Treatment of such an aqueous solution with an aqueous solution of tris(2,2′-bipyridyl)nickel(II) dichloride precipitated a yellow solid for which analytical data most nearly accord with $[Ni(bipy)_3][Os(CO)_4]_2$. From these rather am-

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[1] Part LXV, M. I. Bruce, G. Shaw, and F. G. A. Stone, *J.C.S. Dalton*, 1972, 2094.

[2] R. B. King, *Adv. Organometallic Chem.*, 1964, **2**, 206; *Accounts Chem. Res.*, 1970, **3**, 417.

[3] C. J. Fritchie, R. M. Sweet, and R. Schunn, *Inorg. Chem.*, 1967, **6**, 749.

[4] M. I. Bruce, J. D. Cotton, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2162.

[5] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2758.

[6] F. L'Eplattenier, *Inorg. Chem.*, 1969, **8**, 965.

[7] C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1967, 334.

biguous inferences it is difficult to draw any firm conclusions as to the composition of the reduction product. The treatment of the product with phosphoric acid to release $Os(CO)_4H_2$ in high yield, however, perhaps indicates that mononuclear tetracarbonylosmium species are predominant. Other reactions of the material are more illuminating.

Reactions of the ' anion ' with 2 mol of various halide compounds per g-atom of osmium employed gave $Os(CO)_4X_2$ (X = Me, H_3Ge, Ph_3Sn, Me_3Pb, and $AuPPh_3$) complexes, on occasion associated with minor formation of osmium hydride species $Os(CO)_4(H)X$ (X = Me and H_3Ge). Equimolar reactions of methyl iodide or trimethyltin chloride with the ' anion ' afforded the appropriate hydride $Os(CO)_4(H)X$ (X = Me, $SnMe_3$) in more substantial amounts. Formation of the $Os(CO)_4X_2$ and $Os(CO)_4(H)X$ species can be considered as a consequence of either $Na_2Os(CO)_4$ or $NaHOs(CO)_4$ being the major component of the anion material. If the former predominates then the high yield formation of $Os(CO)_4X_2$ species is readily understandable. The formation of $Os(CO)_4(H)X$ when smaller quantities of halides are used then requires some hydrolysis of an $[Os(CO)_4X]^-$ anion. If, however, $NaHOs(CO)_4$ is a significant component of the anion mixture, which previous data indicates it is, the formation of $Os(CO)_4X_2$ in yields sometimes approaching 100% necessitates the occurrence of a reaction between an intermediate hydride $Os(CO)_4(H)X$ and more halide, with elimination of a hydrogen halide. Precedent for this arises in the reaction [4] of $Ru(CO)_2(PEt_3)_2H_2$ and Me_3SiCl to give $Ru(CO)_2(PEt_3)_2(SiMe_3)_2$, and in the suggestion [6] that $Os(CO)_4(H)Me$ is converted into $Os(CO)_4Me_2$ with methyl iodide. It would therefore appear that in the light of the experimental evidence either $NaHOs(CO)_4$ or $Na_2Os(CO)_4$, and probably both, are formed on sodium reduction of $Os_3(CO)_{12}$ in liquid ammonia. In either event, the anion solid represents an excellent intermediate in the synthesis of tetracarbonylosmium complexes.

Carbonylosmium complexes

Complex	Colour	M.p. (t/°C) (b.p. at 10^{-2} mmHg)	Carbonyl stretching frequencies (cm^{-1}) *	^{1}H N.m.r. (τ) †
$Os(CO)_4(Ph_3Sn)_2$	White	228—231	2024s	
$Os(CO)_4(Me_3Pb)_2$	Yellow	(80—90)	2081m, 2022m, 2010s,sh, 2006s	8·79(1) 8·87(10) §
$Os(CO)_4(Ph_3PAu)_2$	Cream	155—165 (dec.)	2035s, 1966m, 1954vs, 1950sh	
$[Os(CO)_4SnMe_2]_2$	Yellow	194—198	2069s, 2010vs, 2007s,sh	8·97
$Os(CO)_4Me_2$	Colourless	65—66	2126w, 2042vs, 2009s, 1976vw	9·86
$Os(CO)_4(H)Me$	Colourless	<25	2130w, 2060m, 2045vs, 2028s, 1950w ‡	
$Os(CO)_4(H_3Ge)_2$	Colourless	70—72	2118w, 2062sh, 2050s,sh, 2034vs, 1994w	7·10
$Os(CO)_4(H)GeH_3$	Colourless		2134w, 2071m, 2054s, 1960w ‡	

* Measured in cyclohexane with a Perkin-Elmer 257 spectrophotometer. † Benzene solution. ‡ ν_{OsH}. § Relative intensities in parentheses.

Tetracarbonyl(dimethyl)osmium, $Os(CO)_4Me_2$, is formed in 90% yield on treating a suspension of the ' anion ' in liquid ammonia with a two molar ratio of methyl iodide, and was isolated here for the first time in a pure state. I.r. evidence for the formation of traces of $Os(CO)_4(Me)H$ (see below) was also obtained. The stable volatile, and colourless $Os(CO)_4Me_2$ was conveniently handled and purified by high vacuum techniques. Its spectroscopic properties (Table) are essentially as deduced earlier,[6] and are characteristic of a *cis* (C_{2v}) molecular isomer. Formation of $Os(CO)_4Me_2$ in much lower yield was observed when equimolar quantities of methyl iodide and the osmium anion were mixed. Small amounts of a low-melting (<25°) colourless solid were isolated in addition. The i.r. spectrum of this species suggests that it is $Os(CO)_4(H)Me$, having five absorptions in the 2150—1950 cm^{-1} region (Table); the four at highest energy being attributable to the four carbonyl stretching frequencies of a *cis* (C_s) isomer. The weaker absorption at 1950 cm^{-1} is in the region typical of an OsH stretching frequency, and compares with values for $Os(CO)_4(H)SiMe_3$ [8] and $Os(CO)_4(H)GeMe_3$ [9] of 1948 and 1950 cm^{-1} respectively. Unfortunately, the substance decomposed in benzene solution during an attempted study of its n.m.r. spectrum. This instability is consistent with that suggested [6] for $Os(CO)_4(H)Me$, which has, however, not been previously observed.

In order to investigate further the formation of hydrides *via* this anion mixture, the equimolar reaction with Me_3SnCl was studied, since the expected hydride product $Os(CO)_4(H)SnMe_3$ is well characterised.[8] Reaction did indeed afford this hydride, but along with $Os(CO)_4(Me_3Sn)_2$ as the major product. A 2 : 1 molar excess of triphenyltin chloride with the ' anion,' on the other hand, led to unique high-yield formation of $Os(CO)_4(Ph_3Sn)_2$. The anion route is of value here in that the other convenient route to such a complex, namely the thermal reaction of a triorganotin hydride with $Os_3(CO)_{12}$, is precluded by the thermal instability of triphenyltin hydride. White, air-stable $Os(CO)_4(Ph_3Sn)_2$ is similar to its ruthenium analogue in exhibiting only a single strong carbonyl band in the i.r. region, assigned to the E_u mode of a *trans* (D_{4h}) molecular structure.

Formation of lead–osmium bonded complexes *via* lead hydrides is not a practical proposition, and the ' anion ' is therefore valuable in allowing the synthesis of $Os(CO)_4(Me_3Pb)_2$ from trimethyl-lead chloride, albeit in low yield.

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[8] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3147.

[9] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2874.

The yellow, liquid $Os(CO)_4(Me_3Pb)_2$ decomposes slowly in air and is unstable in hydrocarbon solvents in the presence of air. The i.r. spectrum (Table) has four carbonyl absorptions suggestive of a *cis* (C_{2v}) arrangement of the Me_3Pb groups, but the ^1H n.m.r. spectrum (Table) establishes the presence of about 10% of the *trans*-isomer. The Si,[8] Ge,[9] and Sn[8] analogues of $Os(CO)_4(Me_3Pb)_2$ also exist as *cis*/*trans* isomeric mixtures, and it has recently been established[10] that there is a rapid intramolecular interconversion of these isomers.

The air- and solution-stable bis(triphenylphosphinegold)tetracarbonylosmium, $Os(CO)_4(AuPPh_3)_2$, prepared by treating the anion material with triphenylphosphinegold chloride, exhibits the four carbonyl bands of a *cis*-isomer.

The bis(germyl) complex $Os(CO)_4(GeH_3)_2$ is readily prepared in near quantitative yield by treating the anion solid with germyl bromide in tetrahydrofuran. This highly volatile complex, easily manipulated in a high vacuum system, adopts a *cis* isomeric configuration. The single resonance in the ^1H n.m.r. spectrum indicates the presence of one isomer, while the ν_{CO} region of the i.r. spectrum, though obscured to some degree by Ge–H bond stretching vibrations, is consistent with a *cis*-isomer. Dominant bands at 823 and 802 cm^{-1} in the spectrum are assigned to GeH_3 group deformation modes. Traces of a species with an i.r. spectrum consistent with that expected for $Os(CO)_4(H)GeH_3$ (see Experimental section) were observed during the purification of $Os(CO)_4(GeH_3)_2$. The formation[11] of $Fe(CO)_4(SiH_3)_2$ from silyl iodide and the tetracarbonylferrate(—II) anion was also accompanied by trace formation of the monosilyl complex $Fe(CO)_4(H)SiH_3$.

Dialkyltin dihalides have been known[12] for many years to afford four-membered heterocyclic ring complexes $[Fe(CO)_4SnR_2]_2$ when treated with $[Fe(CO)_4]^{2-}$. With the anion material derived from treating $Ru_3(CO)_{12}$ with sodium in liquid ammonia, however, no such species was formed,[5] although the complex $[Ru(CO)_4SnMe_2]_2$ is stable and has been prepared by another route.[13] From dimethyltin dichloride and the carbonylosmium ' anion ' the stable, yellow and crystalline $[Os(CO)_4SnMe_2]_2$ is obtained in good yield. The three ν_{CO} bands in the i.r. spectrum are typical of the M_2Sn_2 ring system, and ^1H n.m.r. and mass spectroscopy support the formulation.

EXPERIMENTAL

Mass spectra were measured on an AEI MS 902 instrument operating at 70 V ionising potential, and ^1H n.m.r. spectra with a Varian HA 100 spectrometer. Dodecacarbonyltriosmium was prepared by a literature[7] method. Hydrocarbon solvents were dried by distillation from calcium hydride, and tetrahydrofuran from lithium aluminium hydride. Molecular weights were determined mass spectrometrically. Physical and spectroscopic data for the new compounds are collected in the Table.

Preparation and Reactions of the Carbonylosmium Anion.—The anion-containing solid was typically prepared by suspending $Os_3(CO)_{12}$ (0·1—0·2 g, 0·11—0·22 mmol) in liquid ammonia (*ca.* 30 ml), and adding small pieces of sodium until the blue colour indicative of excess of sodium was just maintained. Removal of this excess by addition of a small amount of the carbonyl compound was followed by evaporation of the ammonia to leave a cream powder which was then suspended in tetrahydrofuran (*ca.* 20 ml).

(a) *With* $[Ni(bipy)_3]Cl_2$. An aqueous solution of $[Ni(bipy)_3]Cl_2$ (0·25 g, 0·35 mmol) was added to a solution of the anion in water (10 ml) prepared from $Os_3(CO)_{12}$ (0·10 g, 0·11 mmol). The yellow precipitate so formed was filtered, washed with water, and dried under high vacuum at room temperature (Found: C, 39·1; H, 3·9; N, 7·4. $C_{38}H_{26}N_6NiO_8Os_2$ requires C, 40·1; H, 2·3; N, 7·4%).

(b) *With* Me_3SnCl. A tetrahydrofuran solution (20 ml) of Me_3SnCl (0·146 g, 0·73 mmol) was added dropwise to a suspension of the anion solid prepared as above from $Os_3(CO)_{12}$ (0·22 g, 0·24 mmol). After the mixture had been stirred for 20 h the solvent was removed (10^{-2} mm) to leave an orange residue which was extracted with hexane. Evaporation gave an orange oil (0·18 g) identified[8] by i.r. and n.m.r. spectroscopy as containing $Os(CO)_4(SnMe_3)_2$ and $Os(CO)_4(H)SnMe_3$ in about 2 : 1 proportion.

(c) *With* Ph_3SnCl. An anion solution obtained from $Os_3(CO)_{12}$ (0·1 g, 0·11 mmol), on treatment (22 h) with a solution of Ph_3SnCl (0·254 g, 0·66 mmol), afforded a yellow residue on removal of solvent. Extraction with dichloromethane gave a cream solid which on recrystallisation from dichloromethane–hexane yielded white *crystals* of $Os(CO)_4(SnPh_3)_2$ (0·24 g, 72%) (Found: C, 48·1; Os, 19·3%; *M*, 1004. $C_{40}H_{30}O_4Sn_2Os$ requires C, 47·9; Os, 19·0%; *M*, 1004).

(d) *With* $Au(PPh_3)Cl$. Reaction (20 h) of $Au(PPh_3)Cl$ (0·33 g, 0·67 mmol) with a quantity of anion derived as in (c) gave a brown residue on removal of solvent. After recrystallisation three times from dichloromethane–hexane cream *crystalline* $Os(CO)_4Au(PPh_3)_2$ (0·155 g, 39%) was obtained (Found: C, 38·3; P, 4·9; Os, 16·2. $C_{40}H_{30}Au_2O_4OsP_2$ requires C, 39·3; P, 5·1; Os, 15·6%).

(e) *With* Me_3PbCl. The anion as in (c) above was treated (19 h) with Me_3PbCl (0·19 g, 0·66 mmol). A hexane extract of the reaction residue remaining after removing tetrahydrofuran afforded a yellow oil. Distillation (80—100°/10^{-2} mm) to a water-cooled probe was accompanied by considerable decomposition, but yielded pale yellow *liquid* $Os(CO)_4(PbMe_3)_2$ (0·06 g, 23%) (Found: C, 15·0; Os, 23·9; Pb, 51·5%; *M*, 808. $C_{10}H_{18}O_4OsPb_2$ requires C, 14·9; Os, 23·6; Pb, 51·4%; *M*, 808).

(f) *With* Me_2SnCl_2. A sample of Me_2SnCl_2 (0·075 g, 0·33 mmol) and the anion prepared as in (c) gave a yellow solution after 20 h. Removal of solvent and sublimation (60—80°/10^{-2} mm) of the residue afforded bright yellow *crystalline* $[Os(CO)_4SnMe_2]_2$ (60 mg, 40%) (Found: C, 16·2; Os, 42·1; Sn, 26·2%; *M*, 904. $C_{12}H_{12}O_8Sn_2Os_2$ requires C, 16·0; Os, 42·2; Sn, 26·3%; *M*, 904).

(g) *With* H_3GeBr. A sample of H_3GeBr (0·32 g, 2·06 mmol) was condensed (—196°) into a tetrahydrofuran (20 ml) suspension of the anion solid generated from $Os_3(CO)_{12}$ (0·20 g, 0·22 mmol); after being warmed to room tempera-

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

[11] B. J. Aylett, J. M. Campbell, and A. Walton, *J. Chem. Soc.* (*A*), 1969, 2110.

[12] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 3833.

[13] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559.

ture the mixture was stirred for 0·5 h. Volatile material was then distilled through traps held at −36 and −196°. In the former a white crystalline solid was retained, and in the latter the solvent. After purification by refractionation, during which traces of a slightly more volatile component were removed, the volatile *solid* was identified as $Os(CO)_4(GeH_3)_2$ (0·29 g, 97%) (Found: C, 10·7; Ge, 32·2; Os, 42·2%; *M*, 454. $C_4H_6O_4Ge_2Os$ requires C, 10·6; Ge, 32·0; Os, 42·0%; *M*, 454).

An i.r. spectrum of the trace of more volatile component observed during purification showed absorptions at 2134, 2071, 2054, and 1960 cm^{-1}, consistent with its being $Os(CO)_4(H)GeH_3$.

(h) *With* CH_3I. (*i*) A suspension of the anion from $Os_3(CO)_{12}$ (0·10 g, 0·11 mmol) in liquid ammonia immediately dissolved on addition of methyl iodide (0·4 ml, 0·91 g, 0·64 mmol) to give a colourless solution. After the mixture had been stirred for 1 h the ammonia was allowed to evaporate, and the residue was fractionated through traps at −45 and −196°. At −45° a white crystalline *solid* condensed and was identified as $Os(CO)_4Me_2$ (0·103 g, 94%) (Found: C, 21·4; Os, 56·9%; *M*, 332. $C_6H_6O_4Os$ requires: C, 21·7; Os, 57·2%; *M*, 332).

(*ii*) Methyl iodide (54 mg, 0·38 mmol) was condensed (−196°) into an ether (10 ml) suspension of a quantity of anion prepared as in (i). After the mixture had been stirred for 1 h the reaction products were fractionated through −78 to −196°. In the former a white solid was collected which melted to a liquid on warming to room temperature. Removal of traces of $Os(CO)_4Me_2$ by refractionation left $Os(CO)_4(H)Me$ (0·01 g, 10%), identified by its i.r. spectrum.

(i) *With* H_3PO_4. To a sample of the solid anion material, prepared from $Os_3(CO)_{12}$ (0·20 g, 0·22 mmol) and dried under high vacuum, phosphoric acid (90%, *ca.* 10 ml) was added dropwise, producing considerable effervescence. When all the solid appeared to be consumed (*ca.* 10 min) volatile material was condensed (−196°) onto P_2O_5 to remove water, and then taken into a −196° trap. In the latter pure $Os(CO)_4H_2$ (0·139 g, 69%) was collected; it was identified by i.r. spectroscopy and by the high-field ^1H n.m.r. signal at τ 18·65. The melting point of $Os(CO)_4H_2$, previously unreported, was measured as in the range −40 to −38°.

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