Chemistry of the Metal Carbonyls. Part LXXI.[1] Carbene(tetracarbonyl)-iron and -osmium Complexes containing Thiazolidinylidene and Related Ligands

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Carbene complexes of Fe^0 and Os^0 have been prepared by treating the appropriate carbonyl anions with 2-chloro-*N*,4-dimethyl-1,3-thiazolium, 2-chloro-*N*-methylpyridinium, and 2-chloro-*N*-methylbenzo-1,3-thiazolium tetrafluoroborates. Treatment of $[M(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$ (M = Fe or Os) with triphenylphosphine affords $[M(CO)_3(PPh_3)\{\overline{CN(Me)C(Me)CHS}\}]$. The osmium complexes $[Os(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$ and $[Os(CO)_4\{\overline{CN(Me){\cdot}C_6H_4{\cdot}S}\}]$ on protonation yield cationic species $[OsH(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]^+$ and $[OsH(CO)_4\{\overline{CN(Me){\cdot}C_6H_4{\cdot}S}\}]^+$, respectively. Analogous methylosmium cationic complexes have been prepared by treating the neutral carbene complexes with trimethyloxonium tetrafluoroborate.

CARBENE complexes of several metals with thiazolidinylidene and pyridinylidene ligands have been prepared either by treating the appropriate carbonylmetal anions with 2-chloro-*N*,4-dimethyl-1,3-thiazolium tetrafluoroborate, (I), or 2-chloro-*N*-methylpyridinium tetrafluoroborate (II),[2] or by oxidative-addition reactions involving the salt (I).[3] The cationic cyclic-carbene or ylide complexes so obtained are related to ruthenium complexes with carbon-bound imidazolium ligands recently reported.[4] Herein we report additional studies on carbene complexes of the type $[M(CO)_4(\text{cyclic carbene})]$ (M = Fe or Os), synthesised by treating the tetracarbonylmetal

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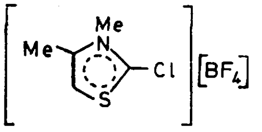
[1] Part LXX, M. Cooke, C. R. Russ, and F. G. A. Stone, *J.C.S. Dalton*, 1975, 256.

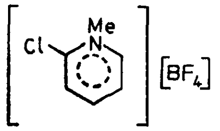
[2] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 760.

[3] P. J. Fraser, W. R. Roper, and F. G. A. Stone, *J. Organometallic Chem.*, 1973, **50**, C54; *J.C.S. Dalton*, 1974, 102.

[4] R. J. Sundberg, R. F. Bryan, I. F. Taylor, and H. Taube, *J. Amer. Chem. Soc.*, 1974, **96**, 381.

dianions of iron or osmium with the salts (I)—(III). Only spectroscopic evidence has been obtained for the existence of analogous ruthenium complexes. A few neutral cyclic-carbene complexes of Fe^0 have been described,[5,6] and relevant to the results described in this paper complex (IV; M = Fe) was characterised earlier.[2] However, related Os^0 complexes have not been hitherto reported. Complexes of platinum and palladium containing the carbene *N*-methylbenzothiazolinylidene have recently been described.[7]


(I)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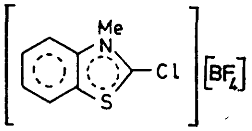
(III)

$[M(CO)_4\{CN(Me)C(Me)CHS\}]$
(IV) M = Fe, Ru, or Os

$[M(CO)_4\{CN(Me)\cdot C_6H_4\cdot S\}]$
(V) M = Fe or Os

$[M(CO)_4\{CN(Me)CHCHCHCH\}]$
(VI) M = Fe or Ru

$[M(CO)_3(PPh_3)\{CN(Me)C(Me)CHS\}]$
(VII) M = Fe or Os

$[OsH(CO)_4\{CN(Me)C(Me)CHS\}]X$
(VIII) X = BF_4 or PF_6

$[OsH(CO)_4\{CN(Me)\cdot C_6H_4\cdot S\}][BF_4]$
(IX)

$[OsMe(CO)_4\{CN(Me)C(Me)CHS\}][BF_4]$
(X)

$[OsMe(CO)_4\{CN(Me)\cdot C_6H_4\cdot S\}][BF_4]$
(XI)

RESULTS AND DISCUSSION

Reactions between the salts (II) and (III) with disodium tetracarbonylferrate–dioxan [8] afforded the complexes (VI) and (V) (M = Fe) respectively. Complex (IV; M = Fe) was also prepared from the ferrate reagent. With the anion from dodecacarbonyltriosmium and sodium in liquid ammonia,[9] the salts (I) and (III) afforded the carbene complexes (IV) and (V) (M = Os), respectively. The new complexes were characterised by analysis (Table 1) and by their i.r. and n.m.r. spectra, data from which are summarised in Table 2. The ruthenium(0) complexes (IV) and (VI) were similarly prepared from $Na_2[Ru(CO)_4]$ [10] and (I) and (II), but attempts to isolate them as crystalline solids failed so that they were only identified by their i.r. spectra which were identical in pattern to their iron and osmium analogues.

The i.r. spectra of all the neutral carbene complexes showed four bands in the carbonyl-stretching region which is consistent with structures (A) or (B). However, the molecular structure has been determined [11] for tetracarbonyl(1,3-dimethylimidazolinylidene)iron(0) by *X*-ray crystallography and shows the carbene ligand to be in the axial position [structure (C)], although the arrangement of the ligands about the iron atom is somewhat distorted from the ideal trigonal-bipyramidal structure. The i.r. data, therefore, do not allow a distinction to be made between the structures (A)—(C), but in view of the *X*-ray result [11] the presence of four ν(CO) bands in

TABLE 1

Carbene complexes of Fe^0 and Os^0

Complex	M.p. (θ_c/°C) [a]	Colour	Yield/%	Analyses [b]/% C	H	N	S
(IV; M = Fe)	77—78	Yellow	40	38·5 (38·5)	2·6 (2·5)	4·9 (5·0)	11·4 (11·4)
(IV; M = Os) [c]	97—100	Yellow	69	25·9 (26·0)	1·8 (1·7)	3·2 (3·4)	7·7 (7·7)
(V; M = Fe) [d]	119—121	Yellow	30	45·9 (45·5)	2·3 (2·2)	4·6 (4·4)	10·2 (10·1)
(V; M = Os) [e]	124—125	Yellow	73	32·4 (31·9)	1·8 (1·6)	2·9 (3·1)	8·0 (7·1)
(VI; M = Fe) [f]	91—94	Yellow	48	46·3 (46·0)	3·0 (2·7)	5·3 (5·4)	
(VII; M = Fe)	120 [g]	Yellow	54	61·4 (60·6)	4·1 (4·3)	2·9 (2·7)	7·7 (6·2)
(VII; M = Os) [h]	200 [g]	Yellow	58	48·2 (48·1)	3·6 (3·4)	2·2 (2·2)	5·2 (4·9)
(VIII; X = BF_4)	136 [g]	White	95	21·4 (21·5)	1·7 (1·6)	2·7 (2·8)	6·1 (6·4)
(VIII; X = PF_6)	115—118	Pale yellow	59	19·5 (19·3)	1·6 (1·4)	2·6 (2·5)	5·7 (5·7)
(IX)	182—184	White	54	27·0 (26·7)	1·7 (1·5)	2·5 (2·6)	5·9 (6·0)
(X)	170—174	Pale yellow	55	22·9 (23·2)	2·0 (2·0)	2·7 (2·7)	5·9 (6·2)
(XI)	191—193	Pale yellow	55	27·9 (28·2)	1·9 (1·8)	2·7 (2·5)	6·2 (5·8)

[a] *In vacuo*. [b] Calculated values are given in parentheses. [c] *M* (mass spec.) 417 (calc. 415). [d] *M* 317 (calc. 317). [e] *M* 453 (calc. 452). [f] *M* 261 (calc. 261). [g] With decomposition. [h] *M* 651 (calc. 650).

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[5] D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert *Chem. Soc. Rev.*, 1973, **2**, 99.

[6] D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

[7] D. J. Cardin, B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

[8] J. P. Collman and N. W. Hoffman, *J. Amer. Chem. Soc.* 1973, **95**, 2689 and refs. therein.

[9] R. D. George, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 972.

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

[11] G. Huttner and W. Gratzke, *Chem. Ber.*, 1972, **105**, 2714.

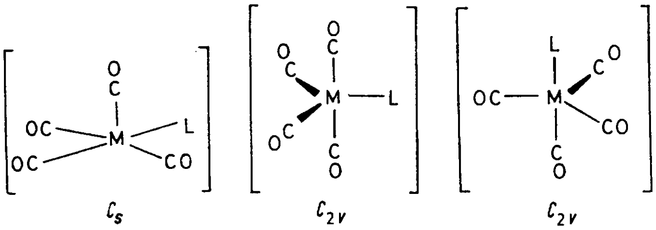
Table 2

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

Complex	ν_{CO}/cm^{-1}	Solvent	Chemical shift (τ)		Solvent
(IV; M = Fe)	2 045s, 1 968m, 1 938vs, 1 929vs	Cyclohexane *	C–*Me*	7·43(d)	$(CD_3)_2CO$
				[*J*(HH) 1·0 Hz]	
			N–*Me*	5·83(s)	
			C–*H*	2·60(s)	
(IV; M = Ru)	2 050s, 1 974m, 1 942vs, 1 933vs	Cyclohexane			
(IV; M = Os)	2 055s, 1 970m, 1 933s, 1 925s	Cyclohexane	C–*Me*	7·52(s)	$CDCl_3$
			N–*Me*	5·97(s)	
			C–*H*	2·98(s)	
(V; M = Fe)	2 046s, 1 975m, 1 945vs, 1 937vs	Hexane	N–*Me*	5·58(s)	$(CD_3)_2CO$
			C_6H_4	2·52(m)	
				2·13(m)	
(V; M = Os)	2 054s, 1 973m, 1 934s, 1 929s	Cyclohexane	N–*Me*	5·72(s)	$CDCl_3$
			C_6H_4	2·47(m)	
(VI; M = Fe)	2 039s, 1 962m, 1 932vs, 1 920vs	Cyclohexane	N–*Me*	5·45(s)	$(CD_3)_2CO$
			C_5H_4N	2·60(m)	
				1·35(m)	
(VI; M = Ru)	2 046s, 1 970m, 1 937vs, 1 925vs	Hexane			
(VII; M = Fe)	1 869	Benzene	C–*Me*	8·83(s)	C_6D_6
			N–*Me*	6·33(s)	
			C–*H*	4·24(s)	
			P*Ph*$_3$	2·87(m)	
(VII; M = Os)	1 870	Benzene	C–*Me*	8·83(s)	C_6D_6
			N–*Me*	6·53(s)	
			C–*H*	4·28(s)	
			P*Ph*$_3$	2·96(m)	
(VIII; X = BF_4)	2 166m, 2 099s, 2 078vs	Nitromethane	Os–*H*	17·02(s)	$(CD_3)_2CO$
			C–*Me*	7·38(s)	
			N–*Me*	5·77(s)	
			C–*H*	2·32(s)	
(VIII; X = PF_6)	2 165w, 2 101m, 2 079vs	Nitromethane	Os–*H*	16·97(s)	$(CD_3)_2CO$
			C–*Me*	7·35(s)	
			N–*Me*	5·72(s)	
			C–*H*	2·23(s)	
(IX)	2 166w, 2 103m, 2 081s	Nitromethane	Os–*H*	16·90(s)	$(CD_3)_2CO$
			N–*Me*	5·40(s)	
			C_6H_4	2·27(m)	
				1·77(m)	
(X)	2 159m, 2 085(sh), 2 075vs, 2 053s	Nitromethane	Os–*Me*	9·48(s)	$(CD_3)_2CO$
			C–*Me*	7·30(s)	
			N–*Me*	5·68(s)	
			C–*H*	2·20(s)	
(XI)	2 160m, 2 089(sh), 2 076vs, 2 058s	Nitromethane	Os–*Me*	9·37(s)	$(CD_3)_2CO$
			N–*Me*	5·47(s)	
			C_6H_4	2·32(m)	
				1·85(m)	

* In tetrahydrofuran solution, the two low-frequency absorptions appear as a single band (ref. 2).

the spectra of (IV)—(VI) might imply structure (B) in solution. All of the neutral carbene complexes which we prepared would be expected to exhibit stereochemical non-rigidity at ambient temperature due to intramolecular exchange of the ligands about the central metal atom.[12] Unfortunately, even for the osmium complexes, ligand permutations are very rapid and n.m.r. spectra corresponding to a 'frozen' configuration were not obtained. The ^{13}C n.m.r. spectrum of the osmium complex (IV) showed a single sharp peak even at −90 °C, measured at −193 p.p.m. (relative to Me_4Si), and assignable [13] to the CO ligands.



(A) (B) (C)

M = Fe, Ru, or Os ; L = carbene ligand.

With triphenylphosphine, complexes (IV; M = Fe and Os) underwent simple substitution to give the tricarbonyl species (VII). In the carbonyl-stretching region the i.r. spectra of these complexes showed a single strong band (Table 2), which suggests that the phosphine and carbene ligands are *trans* to one another. Complex (VII; M = Fe) is the only neutral carbene complex which we have prepared which does not show the parent molecular ion in its mass spectrum. We obtained no identifiable product from the reaction of (IV; M = Os) with pyridine, although reactions of this nucleophile

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[12] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266.

[13] B. E. Mann, *Adv. Organometallic Chem.*, 1974, **12**, 135 and refs. therein.

with carbonylmetal–carbene complexes generally result in displacement of the carbene ligand rather than one of the carbonyl groups.[14]

The osmium(0) complexes (IV) and (V) undergo a limited number of oxidative-addition reactions. With tetrafluoroboric acid in acetic anhydride they reacted readily to give the hydridometal tetrafluoroborate salts (VIII) and (IX), respectively. In the n.m.r. spectrum the hydride resonances (Table 2) are in the expected region for terminal Os–H ligands.[15] At room temperature, in acetonitrile solution, these salts reacted instantly with triethylamine to regenerate (IV) and (V) (M = Os). With nitrosonium hexafluorophosphate in a mixture of methanol and toluene, (IV; M = Os) did not undergo straightforward oxidative addition but gave the hydrido-complex (VIII; X = PF_6). This is analogous to the reaction of $[M(CO)_3(PPh_3)_2]$ (M = Ru or Os) with $[NO][PF_6]$ in the same solvent mixture to give $[HM(CO)_3(PPh_3)_2][PF_6]$.[16] The analogy does not extend to the iron complexes; under the same conditions complex (IV; M = Fe) decomposed and no formation of the expected $[Fe(CO)_3NO\{\overline{CN(Me)C(Me)CHS}\}][PF_6]$ was observed. When the reactions between $[NO][PF_6]$ and (IV; M = Os) were carried out in non-protic solvents (CH_2Cl_2 or MeCN), decomposition was observed and no nitrosyl derivatives were isolated. Complexes (IV) and (V) (M = Os) readily reacted with trimethyloxonium tetrafluoroborate in methylene chloride to give respectively the Os^{II} complexes (X) and (XI). The methyl proton resonances (Table 2) are in the expected region for methyl groups bonded directly to the metal.[17] However, only the hydrido-complexes (VIII) and (IX) could be isolated from the analogous reaction of (IV) and (V) (M = Os) with triethyloxonium tetrafluoroborate. Presumably the osmium–ethyl complexes are formed as unstable intermediates which undergo β elimination[18] to form the hydrido-complex and ethylene.

Whether the ligands H or Me in (VIII)—(XI) are *cis* or *trans* to the carbene group was not established with certainty. Insufficiently concentrated solutions were obtained for the ^{13}C carbonyl-carbon resonances to be observed, but the i.r. spectra in the carbonyl-stretching region (Table 2) indicate a *cis*-arrangement of the ligands. Attempts to prepare similar Os^{II}–methyl complexes by reaction of the neutral carbene complexes with methyl iodide or methyl fluorosulphonate were unsuccessful.

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian T60 and HA100 spectrometers, i.r. spectra with Perkin-Elmer 257 and 457 spectrophotometers, and mass spectra with an A.E.I. MS902 spectrometer operating at 70 eV ionisation potential.* Solvents were dried and distilled under nitrogen before use and all reactions were carried out under oxygen-free nitrogen.

The anions $[Ru(CO)_4]^{2-}$ and $[Os(CO)_4]^{2-}$ were prepared as described elsewhere.[9,10] ' Collman's reagent ' $Na_2[Fe(CO)_4]\cdot C_4H_8O_2$ was obtained from Ventron Corporation Alfa Products. 2-Chloro-*N*,4-dimethyl-1,3-thiazolium, (I),[2] 2-chloro-*N*-methylpyridinium, (II),[2] and 2-chloro-*N*-methylbenzo-1,3-thiazolium, (III),[19] tetrafluoroborates were prepared as described elsewhere.

Synthesis of the Carbene Complexes.—(a) *Tetracarbonyl*(N,4-*dimethyl*-1,3-*thiazolidin*-2-*ylidene*)*iron*(0) $[Fe(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$, (IV). This was prepared by treating $Na_2[Fe(CO)_4]\cdot C_4H_8O_2$ (0·578 g, 1·91 mmol) in tetrahydrofuran (40 cm^3) at −30 °C with (I) (0·487 g, 2·07 mmol). After warming to room temperature, the mixture was stirred for 1 h and filtered through Kieselguhr under nitrogen. The filtrate was evaporated under reduced pressure to give a dark red oil which was extracted with hexane (50 cm^3). The hexane extract was concentrated to *ca*. 5 cm^3 by slow evaporation under reduced pressure and the supernatant liquid was decanted from the crystals which had been deposited. The product (IV) was recrystallised from hexane at −20 °C.

(b) *Tetracarbonyl*(N-*methylbenzo*-1,3-*thiazolidin*-2-*ylidene*)-*iron*(0), $[Fe(CO)_4\{\overline{CN(Me)\cdot C_6H_4\cdot S}\}]$, (V). This was prepared by treating $Na_2[Fe(CO)_4]\cdot C_4H_8O_2$ (0·583 g, 1·93 mmol) in tetrahydrofuran (40 cm^3) at −30 °C with (III) (0·552 g, 2·01 mmol) and proceeding as for complex (IV) in (*a*) above.

(c) *Tetracarbonyl*(N-*methylpyridin*-2-*ylidene*)*iron*(0), $[Fe(CO)_4\{\overline{CN(Me)CHCHCHCH}\}]$, (VI). This was prepared by treating $Na_2[Fe(CO)_4]\cdot C_4H_8O_2$ (1·005 g, 3·33 mmol) in tetrahydrofuran (40 cm^3) at −30 °C with (II) (0·743 g, 3·45 mmol) and proceeding as in (*a*) above.

(d) $[Os(CO)_4\{\overline{CN(Me)C(Me)CHS}\}]$, (IV; M = Os). This was prepared by treating $Na_2[Os(CO)_4]$ [obtained by the reaction of $Os_3(CO)_{12}$ (0·278 g, 0·95 mmol Os) with sodium metal in liquid ammonia] in tetrahydrofuran (40 cm^3) at −30 °C with (I) (0·237 g, 1·00 mmol). After warming to room temperature, the mixture was stirred overnight and filtered through Kieselguhr under nitrogen. The filtrate was evaporated under reduced pressure to give an orange oil which, on addition of light petroleum (b.p. 30—40 °C) (50 cm^3) and cooling to −78 °C, gave a yellow solid. *Crystals* were obtained from dichloromethane–hexane. The complex $[Os(CO)_4\{\overline{CN(Me)\cdot C_6H_4\cdot S}\}]$ (V; M = Os) was similarly prepared using (III) and crystallised from hexane at −20 °C.

Reactions of the Carbene Complexes.—(a) *With triphenylphosphine*. The complex $[Fe(CO)_3(PPh_3)\{\overline{CN(Me)C(Me)CHS}\}]$ (VII) was prepared by heating under reflux a solution of (IV) (0·226 g, 0·81 mmol) in light petroleum (b.p. 100—120 °C) (50 cm^3) with triphenylphosphine (0·222 g, 0·85 mmol) for 8 h. The solution darkened and, on cooling to room temperature, gave a brown precipitate which was filtered off and washed with ether. The residue was dissolved in benzene (50 cm^3) at room temperature and the resulting solution was filtered through Kieselguhr under nitrogen. Addition of hexane to the filtrate gave yellow

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* 1 eV ≈ 1·60 × 10^{-19} J.

[14] E. O. Fischer, B. Heckel, and H. Werner, *J. Organometallic Chem.*, 1971, **28**, 359.

[15] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

[16] B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1972, 1268.

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

[18] G. Wilkinson, *Pure and Appl. Chem.*, 1972, **30**, 627.

[19] C. H. Game, Ph.D. Thesis, Bristol University, 1974.

crystals. The product was recrystallised from benzene–hexane. The analogous osmium complex was similarly prepared but the reaction was complete after only 2 h refluxing.

(b) *With tetrafluoroboric acid.* The complex $[\mathrm{OsH(CO)_4\{\overline{CN(Me)C(Me)CHS}\}][BF_4]}$, (VIII), was prepared by adding a mixture (5 $\mathrm{cm^3}$) of tetrafluoroboric acid solution and acetic anhydride (1 : 2 v/v) to complex (IV; M = Os) (0·109 g, 0·26 mmol). The resulting yellow solution was filtered through Kieselguhr and diethyl ether was added to the filtrate until precipitation of the white *crystals* was complete. The product was recrystallised from acetonitrile–diethyl ether. The complex $[\mathrm{OsH(CO)_4\{\overline{CN(Me){\cdot}C_6H_4{\cdot}S}\}][BF_4]}$, (IX), was similarly prepared from (V; M = Os).

(c) *With nitrosonium hexafluorophosphate.* Complex (VIII; X = $\mathrm{PF_6}$) was prepared by adding excess of solid $\mathrm{[NO][PF_6]}$ (0·033 g, 0·19 mmol) to a suspension of (IV; M = Os) (0·063 g, 0·15 mmol) in toluene (5 $\mathrm{cm^3}$)–methanol (1 $\mathrm{cm^3}$). Pale yellow *crystals* were immediately formed.

(d) *With trimethyloxonium tetrafluoroborate.* The complex $[\mathrm{OsMe(CO)_4\{\overline{CN(Me)C(Me)CHS}\}][BF_4]}$, (X), was prepared by adding a large excess of solid trimethyloxonium tetrafluoroborate (0·392 g, 2·65 mmol) to a solution of (IV; M = Os) (0·113 g, 0·27 mmol) in freshly distilled dichloromethane (15 $\mathrm{cm^3}$). The solution changed from orange to pale yellow over 20 min. After stirring for 4 h the mixture was filtered to remove excess of $\mathrm{[Me_3O][BF_4]}$ and diethyl ether was added to the filtrate until precipitation of the yellow solid was complete. Pale yellow *crystals* were obtained from acetonitrile–diethyl ether. The complex $[\mathrm{OsMe(CO)_4\{\overline{CN(Me){\cdot}C_6H_4{\cdot}S}\}][BF_4]}$, (XI), was similarly prepared from (V; M = Os).

(e) *With triethyloxonium tetrafluoroborate.* The salt $\mathrm{[Et_3O][BF_4]}$ (0·084 g, 0·44 mmol) was added to a solution of (V; M = Os) (0·200 g, 0·44 mmol) in dichloromethane (10 $\mathrm{cm^3}$). After stirring for 3 h at room temperature the mixture was filtered. The filtrate was evaporated under reduced pressure to give a yellow solid residue which was dissolved in dichloromethane and the solution filtered through Kieselguhr. Diethyl ether was added to the filtrate until no further precipitation of yellow powder occurred. The precipitate (0·090 g, 37·7%) was identified (^{1}H n.m.r. and i.r. spectrum) as the hydrido-complex, (IX).

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