Fluorocarbon Complexes of the Transition Metals. Part III.[1] Chemistry of Tertiary Arsine Derivatives of Tetrakis(trifluoromethyl)rhodacyclopentadiene

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The five-co-ordinate rhodacyclopentadiene complexes $[RhClL_2C_4(CF_3)_4]$ [L = $AsMe_3$, $AsMe_2Ph$, or $AsMe_2(p\text{-}MeOC_6H_4)$] react readily with a variety of neutral ligands to give six-co-ordinate species $[RhClL'L_2C_4(CF_3)_4]$ [L′ = py, NH_3, MeCN, $PHPh_2$, $P(OMe)_3$, $AsMe_3$, or $P(OCH_2)_3CC_2H_5$]. The corresponding six-co-ordinate carbonyl complexes $[Rh(CO)ClL_2C_4(CF_3)_4]$ react with silver salts to produce $[Rh(CO)XL_2C_4(CF_3)_4]$ (X = $CF_3CO_2^-$ or ClO_4^-) or $[RhXL_2C_4(CF_3)_4]$ (X = $CH_3CO_2^-$ or $p\text{-}MeC_6H_4SO_3^-$). These same complexes also react with [Tl(dike)] to give $[Rh(dike)L_2C_4(CF_3)_4]$ [dike = acetylacetonate(acac) or hexafluoroacetylacetonate(hfac)]. Treatment of $[RhCl(CO)L_2C_4(CF_3)_4]$ with $AgClO_4$ followed by a neutral ligand gives the complexes $[RhL_2'L_2C_4(CF_3)_4][ClO_4]$ [L′ = MeCN or $P(OMe)_3$; L_2' = diars]. In the complexes $[RhClL'L_2C_4(CF_3)_4]$ (L′ = py, MeCN, $AsMe_3$, or H_2O), L′ undergoes exchange in solution at 30 °C. Static six-co-ordinate structures for these complexes can be achieved at low temperatures. The ^1H and ^{19}F spectra of these complexes over a range of temperatures were measured and the results are discussed. I.r. and ^1H and ^{19}F n.m.r. spectra of the remaining complexes are also discussed.

We have previously shown that the chlorine and carbonyl ligands in the rhodacyclopentadienes $[Rh(CO)ClL_2C_4(CF_3)_4]$ (L = $AsMe_3$ or $AsMe_2Ph$) are labile [1,2] and that in two related complexes one rhodium–carbon bond is longer and presumably weaker than the other.[3,4] We further find that derivatives of tetrakis(trifluoromethyl)rhodacyclopentadiene catalyze the cyclotrimerization of hexafluorobut-2-yne [2] and note that metallocyclopentadienes have been postulated as intermediates in certain metal-catalyzed acetylene cyclotrimerizations.[5a–c] These observations suggest that a co-ordination–insertion sequence involving the rhodacycle and a third molecule of the acetylene could be one of the final steps in the cyclotrimerization process. As part of our study of this reaction we have investigated the ability of the rhodacycle to bind additional ligands and its stability under a variety of conditions.

EXPERIMENTAL

All solvents were appropriately dried and distilled before use and were stored under an atmosphere of prepurified nitrogen. Although the complexes prepared appear to be stable to air and moisture, all preparations were routinely performed under nitrogen. Light petroleum has b.p. 30—60 °C. ^{19}F N.m.r. spectra were obtained on a JEOL C-60HL spectrometer while a JEOL MH-100 instrument was used to obtain ^1H spectra. ^{19}F Chemical shifts are referred to ααα-trifluorotoluene (0·0 p.p.m.) and are increasing to high field. ^1H Chemical shifts are expressed in τ. Temperature calibration for the variable-temperature n.m.r. studies was achieved by measuring the chemical shift difference of a sample of pure methanol. I.r. spectra were obtained on a Beckman IR-18A spectrophotometer using Nujol mulls unless otherwise specified. Conductance measurements were obtained on a Thomas–Serfass model RCM 15 B1 instrument and a conventional cell which had been calibrated with 0·02M-aqueous potassium chloride. The starting rhodacycles were prepared as described previously.[1]

Three general methods were used to prepare the complexes reported here. A typical example of each is given below.

$[RhClL'L_2C_4(CF_3)_4]$ *Complexes*.—The appropriate six-co-ordinate carbonyl complex $[Rh(CO)ClL_2C_4(CF_3)_4]$ (0·34 mmol) was dissolved in benzene (10 ml) and the solution was refluxed under nitrogen for 3 h until it was bright yellow. The solution was concentrated to *ca.* 4 ml under reduced pressure and a two-fold excess of the desired ligand was added. Crystallization was induced by dilution with light petroleum and cooling to 0 °C. The crude complex was recrystallized from chloroform–light petroleum and obtained in quantitative yield.

$[RhXL_2C_4(CF_3)_4]$ *and* $[Rh(CO)XL_2C_4(CF_3)_4]$ *Complexes*.—A solution of $[Rh(CO)ClL_2C_4(CF_3)_4]$ (0·34 mmol) in benzene–ethanol (1 : 1, v/v) (20 ml) was treated with an ethanol solution of the appropriate silver salt (0·34 mmol) under nitrogen. The mixture was stirred in the dark for 1—2 h and was then filtered through a pad of diatomaceous earth. The pale yellow filtrate was concentrated to *ca.* 5 ml and crystallization induced by dilution with diethyl ether and cooling to 0 °C. The crude product was recrystallized from acetone–diethyl ether in quantitative yield.

$[RhL_2'L_2C_4(CF_3)_4][ClO_4]$ *Complexes*.—A solution of $[Rh(CO)ClL_2C_4(CF_3)_4]$ (0·34 mmol) in benzene–ethanol (1 : 1, v/v) (20 ml) was treated with an ethanolic solution of $AgClO_4$ (0·070 g, 0·34 mmol). The mixture was stirred in the dark for 2 h and was then filtered through a pad of diatomaceous earth. Following concentration of the filtrate to *ca.* 5 ml under reduced pressure a two-fold excess of the desired ligand was added and crystallization was induced by dilution with diethyl ether and cooling to 0 °C. The crude complex was recrystallized from acetone–diethyl ether and obtained in quantitative yield. Although no difficulty has been encountered in our handling of these complexes (*e.g.* grinding or heating to over 200 °C did not cause detonation), as with any perchlorate, due care should be exercised when handling them.

Acetylacetonatobis(trimethylarsine)rhodatetrakis(trifluoromethyl)cyclopentadiene, $[Rh(acac)(AsMe_3)_2C_4(CF_3)_4]$.—A benzene solution (10 ml) of $[Rh(CO)Cl(AsMe_3)_2C_4(CF_3)_4]$ (0·25 g, 0·34 mmol) was treated with freshly prepared thallium(I) acetylacetonate (0·1 g, 0·34 mmol) at room temperature. After being stirred for 3 h the mixture was filtered through a pad of diatomaceous earth and the filtrate was concen-

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[1] Part II, J. T. Mague, M. O. Nutt, and E. H. Gause, *J.C.S. Dalton*, 1973, 2578.

[2] E. H. Gause, Ph.D. Thesis, Tulane University, 1973.

[3] J. T. Mague, *Inorg. Chem.*, 1970, **9**, 1610.

[4] J. T. Mague, *Inorg. Chem.*, 1973, **12**, 2649.

[5] (*a*) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, 1967, **89**, 844; (*b*) K. Moseley and P. M. Maitlis, *J.C.S. Dalton*, 1974, 169; (*c*) W. H. Baddley and G. B. Tupper, *J. Organometallic Chem.*, 1974, **67**, C16.

trated to *ca.* 5 ml under reduced pressure. Dilution with light petroleum and cooling to 0 °C, afforded the product as light pink crystals which were recrystallized from chloroform–light petroleum.

Hexafluoroacetylacetonatobis(trimethylarsine)rhodatetrakis(trifluoromethyl)cyclopentadiene $[Rh(hfac)(AsMe_3)_2C_4(CF_3)_4]$.—To a solution of $[Rh(CO)Cl(AsMe_3)_2C_4(CF_3)_4]$ (0·25 g, 0·34 mmol) in acetone (10 ml) was added thallium(I) hexafluoroacetylacetonate (0·146 g, 0·34 mmol). The mixture was stirred for *ca.* 3 h and then filtered as described above. Concentration of the filtrate under reduced pressure followed by dilution with light petroleum and cooling to 0 °C afforded the product as light yellow crystals which were recrystallized from acetone–light petroleum.

Carbonylbis[dimethyl(p-methoxyphenyl)arsine]perchloratorhodatetrakis(trifluoromethyl)cyclopentadiene, $[Rh(OClO_3)(CO)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4]$.—A solution of $[Rh(CO)Cl\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4]$ (0·24 g, 0·26 mmol) in benzene–ethanol (1 : 1, v/v) (20 ml) was treated with silver perchlorate (0·054 g, 0·26 mmol) in ethanol and the mixture was stirred at room temperature for 2 h followed by filtration through a pad of diatomaceous earth and concentration of the filtrate to *ca.* 5 ml under reduced pressure. Carbon monoxide was passed through the solution while light petroleum was added. Upon cooling to 0 °C the product precipitated as pale yellow needles which were filtered off and recrystallized from acetone–diethyl ether–light petroleum.

TABLE 1

Analytical data

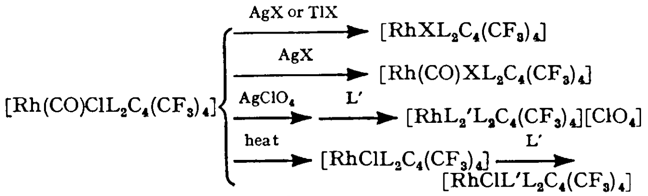
Complex		Found (%)					Calc. (%)					M.p.
		C	H	N	Cl	F	C	H	N	Cl	F	(t/°C) ‡
(I)	$[Rh(O_2CCH_3)(AsMe_2Ph)_2C_4(CF_3)_4]$	36·55	2·5			25·3	36·72	2·79			26·30	198
(II)	$[Rh(O_2CCH_3)(AsMe_3)_2C_4(CF_3)_4]$	26·6	2·85			27·4	26·46	2·92			31·40	217
(III)	$[Rh(p\text{-}MeC_6H_4SO_3)(AsMe_2Ph)_2C_4(CF_3)_4]$ *	39·75	3·65				36·68	3·04				200
(IV)	$[Rh(acac)(AsMe_3)_2C_4(CF_3)_4]$	29·5	3·3			28·75	29·78	3·30			29·89	235(d)
(V)	$[Rh(hfac)(AsMe_3)_2C_4(CF_3)_4]$	26·35	2·3			36·0	25·09	2·11			37·60	237(d)
(VI)	$[Rh(CO)(O_2CCF_3)(AsMe_2Ph)_2C_4(CF_3)_4]$	34·75	2·35			29·45	34·78	2·38			30·57	176
(VII)	$[Rh(CO)(O_2CCF_3)(AsMe_3)_2C_4(CF_3)_4]$	24·9	2·0			34·4	24·63	2·33			36·53	208(d)
(VIII)	$[Rh(CO)(p\text{-}MeC_6H_4SO_3)(AsMe_3)_2C_4(CF_3)_4]$ †	29·9	3·1				30·50	2·91				140
(IX)	$[Rh(CO)(OClO_3)\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4]$	33·4	2·85		4·05	22·2	33·13	2·68		3·62	23·40	184(d)
(X)	$[Rh(CO)(OClO_3)(AsMe_3)_2C_4(CF_3)_4]$	22·8	2·25		5·15		22·67	2·29		4·46		192(d)
(XI)	$[RhCl(NH_3)(AsMe_2Ph)_2C_4(CF_3)_4]$	34·25	3·0	1·65	3·7		34·08	2·98	1·66	4·19		205(d)
(XII)	$[RhCl(NH_3)(AsMe_3)_2C_4(CF_3)_4]$	23·75	2·95	2·05	5·3		23·37	2·95	1·95	4·93		178(d)
(XIII)	$[RhCl\{P(OMe)_3\}(AsMe_2Ph)_2C_4(CF_3)_4]$	34·15	3·2		4·05		34·11	3·29		3·73		130(d)
(XIV)	$[RhCl(PHPh_2)(AsMe_2Ph)_2C_4(CF_3)_4]$	34·9	3·3		4·35	25·3	35·14	3·30		3·99	25·65	156(d)
(XV)	$[RhCl\{P(OCH_2)_3CC_2H_5\}(AsMe_3)_2C_4(CF_3)_4]$	28·2	3·25		3·65		27·88	3·39		4·10		230(d)
(XVI)	$[RhCl\{P(OCH_2)_3CC_2H_5\}\{AsMe_2(p\text{-}MeOC_6H_4)\}_2C_4(CF_3)_4]$	36·7	3·65		3·9		36·64	3·56		3·38		171
(XVII)	$[RhCl(py)(AsMe_2Ph)_2C_4(CF_3)_4]$	37·85	3·2	1·45	3·75		38·45	3·01	1·55	3·91		110(d)
(XVIII)	$[RhCl(MeCN)(AsMe_2Ph)_2C_4(CF_3)_4]$	36·3	2·95	1·5	4·0		35·98	2·91	1·61	4·09		150(d)
(XIX)	$[RhCl(MeCN)(AsMe_3)_2C_4(CF_3)_4]$	26·1	2·8	1·9	4·95		25·84	2·85	1·88	4·77		157(d)
(XX)	$[RhCl(AsMe_3)_3C_4(CF_3)_4]$	24·9	3·15		4·55		25·38	3·37		4·41		149(d)
(XXI)	$[Rh(MeCN)_2(AsMe_2Ph)_2C_4(CF_3)_4][ClO_4]$	35·0	3·25	2·8	4·15		34·57	2·91	2·88	3·64		220(d)
(XXII)	$[Rh\{P(OMe)_3\}_2(AsMe_3)_2C_4(CF_3)_4][ClO_4]$	24·9	3·65		4·35		26·29	3·46		3·37		181(d)
(XXIII)	$[Rh(diars)(AsMe_3)_2C_4(CF_3)_4][ClO_4]$	27·35	3·0		3·8		27·38	3·26		3·37		232(d)

* Sulphur analysis: Found, 3·2; Calc., 3·33%. † Sulphur analysis: Found, 3·7; Calc., 3·70%. ‡ d Decomposed.

Carbonylperchloratobis(trimethylarsine)rhodatetrakis(trifluoromethyl)cyclopentadiene, $[Rh(CO)(OClO_3)(AsMe_3)_2C_4(CF_3)_4]$.—This complex was prepared in a manner analogous to that used for the previous complex from $[Rh(CO)Cl(AsMe_3)_2C_4(CF_3)_4]$ (0·24 g, 0·33 mmol) and $AgClO_4$ (0·068 g, 0·33 mmol) in benzene–ethanol (1 : 1, v/v). Recrystallization from acetone–diethyl ether–light petroleum gave the product as fine white needles. As with the other perchlorate complexes, no evidence of instability was noted in our handling of these last two complexes. Nevertheless, care should be exercised when working with them.

RESULTS

Four general procedures were used to prepare the derivatives of the metallocycle. These are depicted in the Scheme.



SCHEME

The complexes are thermally quite stable (Table 1) although the $[RhClL'L_2C_4(CF_3)_4]$ species slowly lose L′ when heated.

The reaction of $[Rh(CO)ClL_2C_4(CF_3)_4]$ (L = $AsMe_3$ or $AsMe_2Ph$) with silver salts is rapid. The i.r. spectra (Table 2) of (I) and (II) are consistent with bidentate co-ordination of acetate.[6,7] Treatment of (I) with carbon monoxide (1 atm) in refluxing benzene effects partial conversion into the unidentate acetate complex $[Rh(CO)(O_2CCH_3)(AsMe_2Ph)_2C_4(CF_3)_4]$ identified by its i.r. spectrum [$\nu_{C\equiv O}$ = 2105s; $\nu_{as}(CO_2)$ = 1610s, 1598s, 1590sh, and 1577sh; $\nu_s(CO_2)$ = 1378s (hexachlorobutadiene mull) cm^{-1}]. A pure sample can be obtained by carrying out the reaction of $[Rh(CO)Cl(AsMe_2Ph)_2C_4(CF_3)_4]$ with silver acetate in a carbon monoxide atmosphere. The complex is only stable in the solid state since upon dissolution in deuteriochloroform it evolves carbon monoxide and reverts to (I).

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[6] S. A. Smith, D. M. Blake, and M. Kubota, *Inorg. Chem.*, 1972, **11**, 660.

[7] D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1969, 2610.

TABLE 2

I.r. and n.m.r. spectroscopic data for rhodacyclopentadiene derivatives

Complex	^{19}F [a,c]	^{1}H [b,c]	Assignment	Solvent	Infrared absorption frequencies (in cm^{-1}) [h]
(I)	−5·51m, −10·55m	2·54m 8·22s 8·44s	C_6H_5 C–CH_3 As–CH_3	$CDCl_3$	1582m, 1533s[$\nu_{as}(CO_2)$], 1460vs [$\nu_s(CO_2)$],[d] 1342s, 1269w, 1258w, 1217vs, 1163vs, 1147vs, 1132sh, 1107vs, 1088m, 947m, 811m, 686m, 655sh, and 648m
(II)	−6·01m, −9·36m	8·01s 8·76s	C–CH_3 As–CH_3	$CDCl_3$	1577m, 1530s[$\nu_{as}(CO_2)$], 1462vs [$\nu_s(CO_2)$],[d] 1340s, 1278w, 1260m, 1215vs, 1196vs, 1161vs, 1136vs, 1107vs, 983m, 946m, 832m, 687s, 650m, and 643s
(III)	−6·65m, −11·17m	2·20 (centre of $A_2'B_2'$ pattern) 2·66m 7·62s 8·30s	C_6H_4 C_6H_5 C–CH_3 As–CH_3	$(CD_3)_2CO$	1576m, 1532m, 1342m, 1255sh, 1238s, 1221vs, 1195vs, 1189sh, 1168sh, 1150vs, 1141sh, 1132sh, 1118vs, 1111sh, 1037m, 1015m, 721w, 698m, and 650m
(IV)	−7·74m, −9·24m	4·80s 8·12s 8·94s	$>$C–H C–CH_3 As–CH_3	$CDCl_3$	1595vs($\nu_{CC} + \nu_{CO}$), 1573sh, 1559m, 1536s($\nu_{CC} + \nu_{CO}$), 1517s, 1401m, 1340s, 1264m, 1219vs, 1182vs, 1150vs, 1117vs, 1097sh, 1021w, 981w, 829w, 787w, and 650m
(V)	−7·51m, −9·23m, +13·45s	3·76s 8·69s	$>$C–H As–CH_3	$(CD_3)_2CO$	1642s($\nu_{CC} + \nu_{CO}$), 1590w, 1578w, 1552m, 1530m, 1523sh, 1496s($\nu_{CC} + \nu_{CO}$), 1342s, 1284sh, 1257vs, 1230sh, 1219vs, 1191vs, 1164sh, 1147vs, 1117vs, 1104s, 984m, 834w, 811w, 682m, and 652m
(VI)	−6·48m, −11·13m,[e] +11·45s	2·62m 8·11s, 8·38s	C_6H_5 As–CH_3	$CDCl_3$	2118s($\nu_{C\equiv O}$), 1689s[$\nu_{as}(CO_2)$], 1579w, 1531m, 1420m[$\nu_s(CO_2)$],[d] 1342m, 1256m, 1222vs, 1205sh, 1192vs, 1182sh, 1164vs, 1142vs, 1107s, 1085s, 797m, 734m, 721w, and 651m
(VII)	−7·22m, −9·49m,[e] +11·29s	8·57s	As–CH_3	$CDCl_3$	2106s($\nu_{C\equiv O}$), 1685sh, 1681[$\nu_{as}(CO_2)$], 1580w, 1532m, 1422m[$\nu_s(CO_2)$],[d] 1330s, 1255sh, 1231sh, 1224vs, 1190vs, 1161vs, 1138s, 1122s, 1092s, 986m, 877w, 853w, 833w, 732m, and 649m
(VIII)	−7·48m, −9·73m [e]	2·53 (centre of $A_2'B_2'$ pattern) 8·04s 8·93s	C_6H_4 C–CH_3 As–CH_3	C_6D_6	2126s($\nu_{C\equiv O}$), 1605w, 1581m, 1538m, 1498w, 1335s, 1286m, 1267sh, 1248vs, 1230sh, 1223vs, 1188vs, 1173vs, 1153vs, 1138sh, 1115vs, 1103sh, 1028s, 998vs(ν_{SO}), 986sh, 840sh, 833m, 816s, 688s, and 648s
(IX)	−6·66m, −11·24m	2·90 (centre of $A_2'B_2'$ pattern) 6·23s 8·04s, 8·20s	C_6H_4 C–CH_3 As–CH_3	$CDCl_3$	2140s($\nu_{C\equiv O}$), 1533w, 1334m, 1221vs, 1192vs, 1185sh, 1161vs, 1153sh, 1140vs, 1128sh, 1110s, 1090s, 1011s [$\nu_3(ClO_4)$], 987w, 919m, 720w, and 648m
(X)	−7·03m, −10·06m	8·38s	As–CH_3	$(CD_3)_2CO$	2134s($\nu_{C\equiv O}$), 1582w, 1537m, 1330s, 1270sh, 1261s, 1226vs, 1191vs, 1175sh, 1156vs, 1132vs, 1115vs, 1105sh, 1017vs[$\nu_3(ClO_4)$], 986m, 841w, 834sh, and 648m
(XI)	−7·72m, −9·98m, −12·67m	2·54m 8·22s, 8·66s ~8·6	C_6H_5 As–CH_3 NH_3	$CDCl_3$	3341m(ν_{NH}), 3326sh, 3240w(ν_{NH}), 1605m(δ_{HNH}), 1575m, 1520m, 1332s, 1250sh, 1231sh, 1216vs, 1193sh, 1184vs, 1161sh, 1150vs, 1140vs, 1125sh, 1108s, 1091s, 1073sh, 804m, 718m, and 647m
(XII)	−7·49m, −9·81m, −11·55m	8·63s 8·75s	NH_3 As–CH_3	$CDCl_3$	3306w(ν_{NH}), 3231w(ν_{NH}), 1620m(δ_{HNH}), 1570m, 1527m, 1330s, 1260sh, 1214vs, 1186vs, 1142vs, 1112sh, 1097sh, 978m, 828m, 760m, and 646s
(XIII)	−7·29m, −12·22m, −14·02m	2·66m 6·24d (J_{P-H} = 9·8 Hz) 8·32s, 8·37s	C_6H_5 OCH_3 As–CH_3	$CDCl_3$	1571w, 1520m, 1325s, 1244m, 1215vs, 1190sh, 1179vs, 1158vs, 1135vs, 1122vs, 1112sh, 1104sh, 1084s, 1063vs, 1040vs, 1030sh, 893m, 798w, 782m, 762m, 728m, 714m, and 647s
(XIV)	−7·80m, −11·07m, −12·67m	1·65m, 2·57m 3·79d (J_{P-H} = 349 Hz) 9·13s	C_6H_5 P–H As–CH_3	$CDCl_3$	2418w(ν_{P-H}), 1574m, 1524m, 1485m, 1443s, 1325s, 1286w, 1280w, 1265sh, 1250m, 1216vs, 1188vs, 1178sh, 1158vs, 1129vs, 1107vs, 1088s, 1076sh, 1026w, 980m, 836m, 824w, 760m, 746m, 706s, 696m, and 643m

Table 2 (*Continued*)

Complex	^{19}F [a,c]	^{1}H [b,c]	Assignment	Solvent	Infrared absorption frequencies (in cm^{-1}) [h]
(XV)	−7·66m, −10·68m, −12·06m	5·73d (J_{P-H} = 4·9 Hz) 8·68s 9·16t	OCH_2 As–CH_3 C–CH_3	$CDCl_3$	1568w, 1523m, 1330s, 1280w, 1260sh, 1250sh, 1212vs, 1189vs, 1170sh, 1161vs, 1155sh, 1118vs, 1095m, 978m, 960s, 941s, 856m, 837w, 798s, and 648s
(XVI)	−7·41m, −12·11m, −13·75m	2·98 (centre of $A_2'B_2'$ pattern) 5·80d (J_{P-H} = 4·6 Hz) 6·26s 8·30s, 8·36s 8·80q 9·18t	C_6H_4 OCH_2 OCH_3 As–CH_3 C–CH_2 C–CH_3	$CDCl_3$	1522w, 1330s, 1217vs, 1097vs, 1086vs, 1047sh, 1036vs, 1022s, 1014s, 976m, 958s, 950s, 920w, 912m, 898w, 857m, 829m, 817m, 795s, 785m, and 650s
(XVII) [f]	−6·31m, −12·43m	1·44 (broad) 2·64m 8·36s	C_5H_5N C_6H_5 As–CH_3	$CDCl_3$	1609w, 1583w, 1558w, 1540w, 1516w, 1357m, 1339m, 1246sh, 1213vs, 1196vs, 1167sh, 1156vs, 1150vs, 1137sh, 1125s, 1109s, 1075m, 778m, 720m, and 647m
(XVIII) [f]	−7·28m, −11·31m	2·55m 8·37s 8·45s	C_6H_5 As–CH_3 C–CH_3	$CDCl_3$	2328w($\nu_{C\equiv N}$), 2303w, 1570m, 1528m, 1332s, 1270sh, 1255sh, 1247sh, 1220vs, 1190vs, 1181vs, 1150vs, 1129vs, 1111vs, 1095sh, 1087sh, 1075sh, 920sh, 808m, 751sh, 720m, and 649s
(XIX) [f]	−7·55m, −10·65m	7·67s 8·69s	C–CH_3 As–CH_3	$CDCl_3$	2330w($\nu_{C\equiv N}$), 2320w, 1568m, 1528m, 1334s, 1283w, 1253m, 1221vs, 1190vs, 1160vs, 1148sh, 1130vs, 1116vs, 1088s, 1036w, 978m, 837sh, 830m, and 647s
(XX) [f]	−7·88m, −10·78m	8·57s 8·69s	As–CH_3(eq) [g] As–CH_3(ax)	$CDCl_3$	1572w, 1527m, 1330s, 1262sh, 1235sh, 1223sh, 1215vs, 1188vs, 1166sh, 1156vs, 1148sh, 1130s, 1120vs, 1102s, 1090s, 979w, and 648m
(XXI)	−7·02m, −11·19m	2·54m 7·94s 8·22s	C_6H_5 C–CH_3 As–CH_3	$(CD_3)_2CO$	2331m($\nu_{C\equiv N}$), 2306m($\nu_{C\equiv N}$), 1577m, 1536m, 1334s, 1280m, 1261m, 1231vs, 1217vs, 1203vs, 1189sh, 1159vs, 1145vs, 1131vs, 1111vs, 1097vs, 1024m, 857m, 834w, 822w, 808m, 719m, 650s, and 626s
(XXII)	−7·05m, −12·72m	5·94m 8·56s	OCH_3 As–CH_3	$(CD_3)_2CO$	1565w, 1517m, 1226s, 1217vs, 1193sh, 1186vs, 1158vs, 1133sh, 1121sh, 1103vs, 1086vs, 1064vs, 1045vs, 1033vs, 792m, 773m, 733w, 643m, and 625s
(XXIII)	−7·08m, −15·18m	2·00 (centre of $A_2'X_2'$ pattern) 7·98s 8·55s	C_6H_4 As–CH_3(eq) [g] As–CH_3(ax)	$(CD_3)_2CO$	1566w, 1520m, 1325s, 1297w, 1282w, 1260w, 1240sh, 1215vs, 1188vs, 1160vs, 1142sh, 1090vs, 976w, 882sh, 798w, 780m, 643s, and 625s

[a] ^{19}F Chemical shifts in p.p.m. relative to ααα-trifluorotoluene (0·0 p.p.m.). [b] ^{1}H In τ. [c] m, multiplet; s, singlet; d, doublet; t, triplet; q, quartet. [d] Hexachlorobutadiene mull. [e] Centre of overlapping multiplets. [f] Chemical shifts at 30 °C. [g] eq, equatorial; ax, axial. [h] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

Similarly (II) can be partially carbonylated in chloroform solution under ambient conditions [$\nu_{C\equiv O}$ = 2098s; $\nu_{as}(CO_2)$ = 1611sh and 1598s; $\nu_{as}(CO_2)$ = 1382s (hexachlorobutadiene mull) cm^{-1}].

The i.r. spectra (Table 2) of (VI) and (VII) and their behaviour as non-electrolytes in acetone solution support their formulation as carbonyl derivatives containing unidentate trifluoroacetate.[6] This is further confirmed by the ^{1}H and ^{19}F n.m.r. spectra (Table 2). Thus the ^{1}H spectrum of (VI) shows two resonances for the methyl groups bound to arsenic as noted previously[1] for [Rh(CO)Cl($AsMe_2Ph)_2$-$C_4(CF_3)_4$], a six-co-ordinate complex with two dissimilar equatorial ligands. In contrast to the latter, the chemical shifts of the two trifluoromethyl groups adjacent to the metal (hereafter called α-CF_3) are only slightly different. Because of the considerable overlap of these broad resonances we can only report an average chemical shift but it is clear from an inspection of the spectra that the α-CF_3 groups are not magnetically equivalent as expected for a six-co-ordinate formulation for (VI) and (VII).

Qualitatively, it was observed that (II) is more readily carbonylated than (I) suggesting that in the presence of the more basic $AsMe_3$ there is more electron density on the metal for π back-bonding with the carbonyl group leading to somewhat stronger binding (but *vide infra*). However this increase cannot be large since the difference in $\nu_{C\equiv O}$ between the carbonyl derivatives of (I) and (II) as well as that between (VI) and (VII) is quite small. It has been suggested[8] that the tendency for a carboxylate ligand to be bidentate increases with increasing pK_a of the parent acid since this would lead to increased electron density on the formally 'ketonic' oxygen. Our results are consistent with this view however in the absence of a sixth ligand the trifluoroacetate can function as a bidentate ligand. Thus by refluxing (VI) in benzene (4 h), the carbonyl group is displaced to give [Rh(O_2CCF_3)($AsMe_2Ph)_2C_4(CF_3)_4$] [$\nu_{as}(CO_2)$ = 1609s; $\nu_s(CO_2)$ = 1481m (hexachlorobutadiene mull) cm^{-1}]. It would be of considerable interest to have structural data on [RhX($AsMe_2Ph)_2C_4(CF_3)_4$] (X = O_2CCH_3 and O_2CCF_3) to see if the co-ordination of trifluoroacetate is

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[8] B. Hammond, F. H. Jardine, and A. G. Vohra, *J. Inorg. Nuclear Chem.*, 1971, **33**, 1017.

more unsymmetrical than that of acetate as might be inferred from the foregoing argument.[8]

Another example of the differing abilities of $[RhXL_2C_4(CF_3)_4]$ to bind carbon monoxide is found in the complexes (III) and (VIII). Under the preparative conditions CO is retained only by the $AsMe_3$ complex, It is possible to prepare $[Rh(CO)(p\text{-}MeC_6H_4SO_3)(AsMe_2Ph)_2C_4(CF_3)_4]$ from (III) and carbon monoxide in acetone under ambient conditions ($\nu_{C\equiv O}$ = 2124 cm^{-1}). However, it is in the latter complex that the CO is more labile despite its having the lower $\nu_{C\equiv O}$ which suggests that the previous argument concerning the lability of carbon monoxide may be oversimplified.

Complexes (III) and (VIII) exhibit a measurable conductivity in acetone solution (*ca.* 5 Ω^{-1} cm^2 equiv^{-1}) but as this is less than that exhibited by normal 1 : 1 electrolytes in this solvent by a factor of more than 20 (Table 3), they are considered to be essentially non-electrolytes with co-ordinated toluene-*p*-sulphonate. This is further supported by the ^{19}F n.m.r. spectrum of (VIII) in which the resonance due to the α-CF_3 groups appears as two overlapping multiplets. Because of the extent to which these signals overlap, it is not possible confidently to assign individual chemical shifts and we report only the average value. It is probable that the toluene-*p*-sulphonate moiety functions as a bidentate ligand in (III) although it is difficult to confirm this because so much of the S–O stretching region is obscured by strong C–F absorptions. Nevertheless it is clear from Table 2 that the mode of co-ordination differs between (III) and (VIII). This is supported by the appearance of a band attributable to an S–O stretching vibration in the i.r. spectrum of the carbonyl derivative of (III) at 992 cm^{-1} that is absent in the spectrum of (III) itself.

The formation of (IV) is somewhat slower than the formation of the complexes discussed above presumably because of the low solubility of [Tl(acac)] in benzene. An attempt to prepare (V) in benzene gave only a low yield of impure product. The spectral data (Table 2) for (IV) and (V) are as expected for normal β-diketonate complexes.[9]

Following unsuccessful attempts to prepare ionic derivatives of the rhodacycle of the type $[RhL_2C_4(CF_3)_4]X$ ($X = PF_6^-$ or ClO_4^-) it was found possible to prepare the monocarbonyl complexes (IX) and (X). Although much of the perchlorate region of the i.r. spectrum is obscured by intense C–F absorptions, the data in Table 2 indicate perchlorate co-ordination in the solid state.[10,11] In $CDCl_3$ solution the perchlorate apparently remains co-ordinated as the ^{1}H n.m.r. spectrum of (IX) shows the arsenic methyl groups to be non-equivalent. Also the ^{19}F spectrum of the α-CF_3 groups is quite broad suggesting that these two groups have slightly different chemical shifts. However in acetone solution both (IX) and (X) behave essentially as 1 : 1 electrolytes (Table 3) although Λ_0 is noticeably lower for these complexes than for the ionic perchlorates (*vide infra*) suggesting that the perchlorate remains partially co-ordinated.

The carbonyl ligand in $[Rh(CO)ClL_2C_4(CF_3)_4]$ complexes is labile and can be removed by refluxing the complex in benzene for a few hours in a nitrogen atmosphere.[1] The resulting $[RhClL_2C_4(CF_3)_4]$ complexes readily co-ordinate a variety of Lewis bases to give compounds (XI)—(XX). The ^{19}F n.m.r. spectra of (XI)—(XVI) (Table 2) indicate that these exist as static six-co-ordinate species in solution at room temperature. This is further confirmed in the case of (XI), (XIII), and (XVI) by the observed non-equivalence of the arsenic methyl groups. The data in Tables 1 and 2 for (XI) and (XII) clearly show the presence of the ammonia molecule. For (XI) the chemical shift of the ammonia protons is essentially the same as the higher-field methyl resonance as evidenced by the increased intensity and somewhat broader appearance of this peak. Although (XI) has a static structure in solution, the addition of ammonia appears to lead to exchange since the resonance at τ 8·66 decreases in intensity and a new broad resonance appears at τ 9·18 (free ammonia occurs at τ 9·38 in deuteriochloroform). The remaining spectroscopic data for (XIII)—(XVI) are unexceptional and as expected for the complexes as formulated.

The solution behaviour of (XVIII)—(XX) contrasts with that of the other $[RhClL'L_2C_4(CF_3)_4]$ complexes discussed above in that only two resonances are observed in their ^{19}F n.m.r. spectra and for (XVII) and (XVIII) the arsenic methyl groups are all equivalent (Table 2). From variable-temperature ^{19}F and ^{1}H n.m.r. spectral studies of these complexes it is apparent that with the possible exception of (XX) there is partial dissociation of L′ in solution with rapid exchange occurring. Thus when pale yellow (XVII) is dissolved in deuteriochloroform a bright yellow solution results whose colour is similar to that for the five-co-ordinate parent complex $[RhCl(AsMe_2Ph)_2C_4(CF_3)_4]$. However complete dissociation does not occur since the observed ^{19}F spectrum does not correspond to that of $[RhCl(AsMe_2Ph)_2C_4(CF_3)_4]$ in deuteriochloroform (−5·00 and −10·77 p.p.m.). Also the *ortho*-proton resonance of the pyridine which is the one which can be expected to be the most affected by co-ordination and which is not obscured by the phenyl proton resonance of the arsine ligand occurs *ca.* 0·1 p.p.m. upfield of that for free pyridine. The n.m.r. data supporting the exchange of pyridine in (XVII) at room temperature are presented in Figure 1c,d. The addition of a small amount of pyridine to the solution at room temperature causes the colour to become slightly more pale yellow and the ^{19}F resonances and the pyridine *ortho*-proton resonance to shift to lower fields. The spectra obtained for this system (Figure 1a,b) again show that exchange occurs but that a static six-co-ordinate structure can be achieved at low temperatures.

The solid-state i.r. spectrum of (XVIII) shows the presence of N-co-ordinated acetonitrile. The weak band at 2303 cm^{-1} may be the combination of $\delta(CH_3)$ and ν(C–C) which has been previously observed in some Rh^{III} acetonitrile complexes.[12] The analytical and ^{1}H n.m.r. data clearly show that only one acetonitrile ligand is present. The assignment of the ^{1}H spectrum (Table 2) is confirmed by the absence of the τ 8·45 signal in the spectrum of the product obtained from $[RhCl(AsMe_2Ph)_2C_4(CF_3)_4]$ and CD_3CN and its shift to τ 8·17 when (XVIII) is treated with a small amount of CD_3CN. Because the acetonitrile resonance is significantly different from that of free acetonitrile (*ca.* τ 8·0) we conclude that the acetonitrile is co-ordinated in solution as well although the upfield shift is unexpected since in (XIX)

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[9] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley-Interscience, New York, 1970, pp. 247—256 and refs. therein.

[10] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

[11] A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, 1956, **4**, 404.

[12] R. D. Foust, jun., and P. C. Ford, *Inorg. Chem.*, 1972, **11**, 899.

and other Rh^{III} complexes [12-14] this resonance occurs in the τ 7·4—7·6 region. In the solid state the complex is a very pale pink but in solution at 30 °C in the absence of added acetonitrile it is distinctly yellow which suggests a small degree of dissociation. The equivalence of the arsenic methyl groups and of the α-CF$_3$ groups at 30 °C can be explained by rapid exchange of acetonitrile which, in this case, necessitates at least some dissociation to provide the free ligand. The exchange is confirmed by the n.m.r. data presented in Figure 2. The limiting spectrum is that expected for the static six-co-ordinate structure. As is evident from Figure 2, it is difficult to observe the appearance of the acetonitrile resonance over the full temperature range because of overlap with the resonances of the arsenic methyl groups. However its position changes only slightly if at all suggesting that even at room temperature the extent of dissociation is small. The proton spectrum of [RhCl(CD$_3$CN)(AsMe$_2$Ph)$_2$C$_4$(CF$_3$)$_4$] was also studied over the same temperature range as for (XVIII) in order to avoid the overlap of the acetonitrile and arsenic methyl-group resonances which could obscure some of the details of the latter in the region of their coalescence. These results confirm that no significant details of the arsenic methyl group resonances are in fact obscured in the spectra shown in Figure 2.

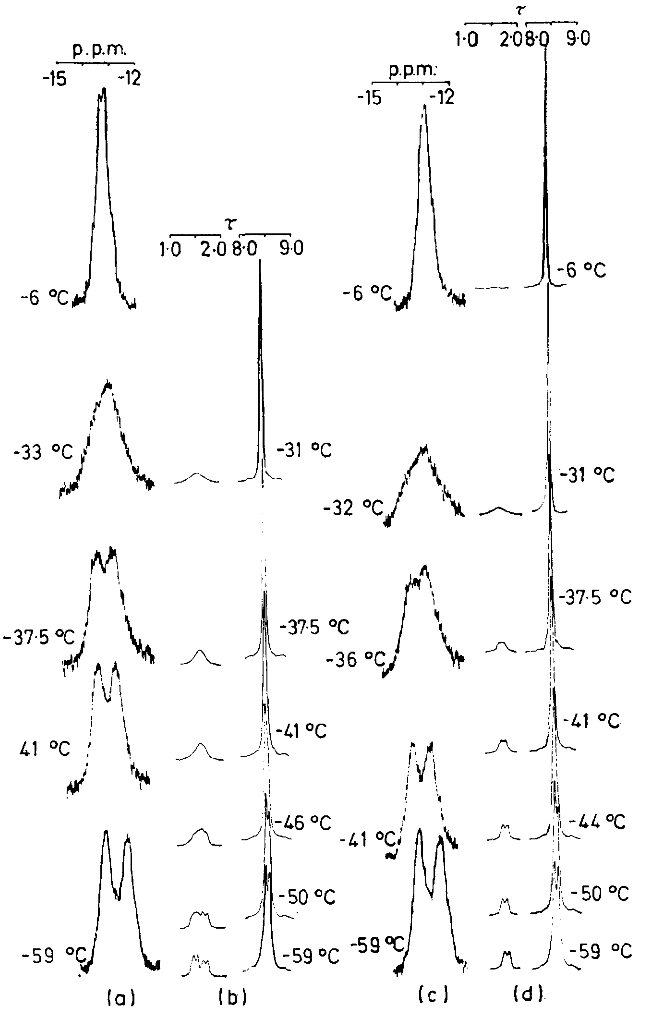

FIGURE 1 N.m.r. spectra of [RhCl(py)(AsMe$_2$Ph)$_2$C$_4$(CF$_3$)$_4$], (XVII), in CDCl$_3$ solution. (a) ^{19}F Spectrum of the α-trifluoromethyl groups, py added. (b) ^{1}H Spectrum in pyridine *ortho*-proton and arsenic methyl-group regions, py added. (c) Same as (a) but without added pyridine. (d) Same as (b) but without added pyridine

When a small amount of acetonitrile is added to a deuteriochloroform solution of (XVIII) at room temperature, the colour changes from pale yellow to nearly colourless and the ^{19}F resonances shift downfield slightly which suggests that the dissociation is repressed. At this temperature, rapid exchange of acetonitrile still occurs (Figure 2) but a static six-co-ordinate structure can again be achieved at low temperature.

Complex (XIX) exhibits similar behaviour with the solid-state i.r. spectrum showing the presence of N-co-ordinated acetonitrile (the weak combination band is also present) while the ^{19}F n.m.r. spectrum shows that exchange of acetonitrile occurs at 30 °C (Table 2). There is evidently a somewhat greater degree of dissociation of acetonitrile here as compared with the previous complex as the acetonitrile resonance shifts from τ 7·67 at 30 °C to τ 7·56 at -20 °C where the static six-co-ordinate structure is achieved (Figure 3). An essentially identical series of spectra are obtained for a solution of (XIX) to which a small quantity of acetonitrile has been added. No coupling of rhodium (^{103}Rh, $I = 1/2$, 100% abundance) to the acetonitrile protons [14] was observed for either (XVIII) or (XIX) even at the lowest temperature studied.

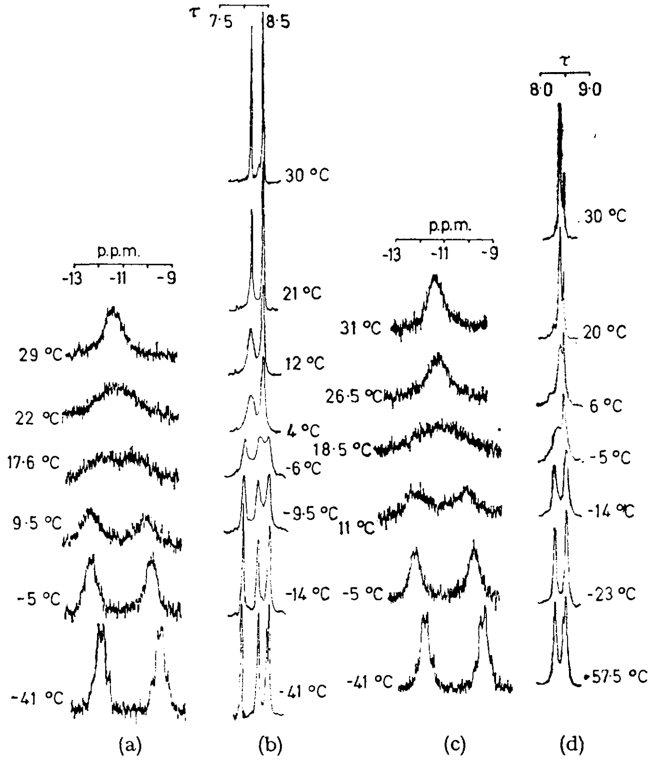

FIGURE 2 N.m.r. spectra of [RhCl(MeCN)(AsMe$_2$Ph)$_2$C$_4$(CF$_3$)$_4$], (XVIII), in CDCl$_3$ solution. (a) ^{19}F Spectrum of the α-trifluoromethyl groups, MeCN added. (b) ^{1}H Spectrum of the acetonitrile and arsenic methyl groups, MeCN added. (c) Same as (a) but without added MeCN. (d) Same as (b) but without added MeCN.

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[13] B. D. Catsikis and M. L. Good, *Inorg. Chem.*, 1969, **8**, 1095.

[14] R. D. Foust, jun., and P. C. Ford, *J. Amer. Chem. Soc.*, 1972, **94**, 5686.

Complex (XX) represents an intermediate case in that in some respects it resembles the systems just discussed and in others it is more reminiscent of $[RhCl(NH_3)(AsMe_2Ph)_2C_4(CF_3)_4]$. The data in Table 2 and the observation that the ^1H n.m.r. spectrum shows no significant change on cooling to −23 °C indicate that (XX) has a static six-co-ordinate structure. In the presence of added trimethylarsine exchange occurs with the equatorial ligand only (Figure 4). The ^{19}F spectrum of (XX) is the same whether or not added trimethylarsine is present and the changes on cooling to −14 °C depicted in Figure 4 also occur in the absence of added ligand. The appearance of only one resonance for the two α-CF_3 groups even at temperatures below that at which the ^1H spectrum indicates that a static six-co-ordinate structure has been achieved is surprising. This is the only complex of the series $[RhClL'L_2C_4(CF_3)_4]$ in which these two trifluoromethyl groups appear to have the same chemical shift within experimental error even when the static six-co-ordinate species is the major one present. Although it is not clear at this point what properties of the equatorial ligands are responsible for determining the chemical shifts of the α-CF_3 groups it appears that in this instance, chlorine and trimethylarsine have essentially the same effect. At first sight, considering the variety of ligands L′ used, we would have expected to find these trifluoromethyl groups to be nonequivalent in the static six-co-ordinate complex as is the case for all the others. The possibility that the observed identity of chemical shifts is due to weak co-ordination of trimethylarsine as a consequence of steric factors does not seem to be valid since, on the basis of the estimated cone angle,[14] the steric properties of trimethylarsine should be intermediate between those of diphenylphosphine and the two phosphite ligands * yet all three of the latter ligands lead to static six-co-ordinate complexes in which the α-CF_3 groups have different chemical shifts. Clearly structural information on (XX) would be desirable to resolve the question of steric effects but in its absence we have no ready explanation for the apparent accidental degeneracy of the chemical shifts of these α-CF_3 groups.

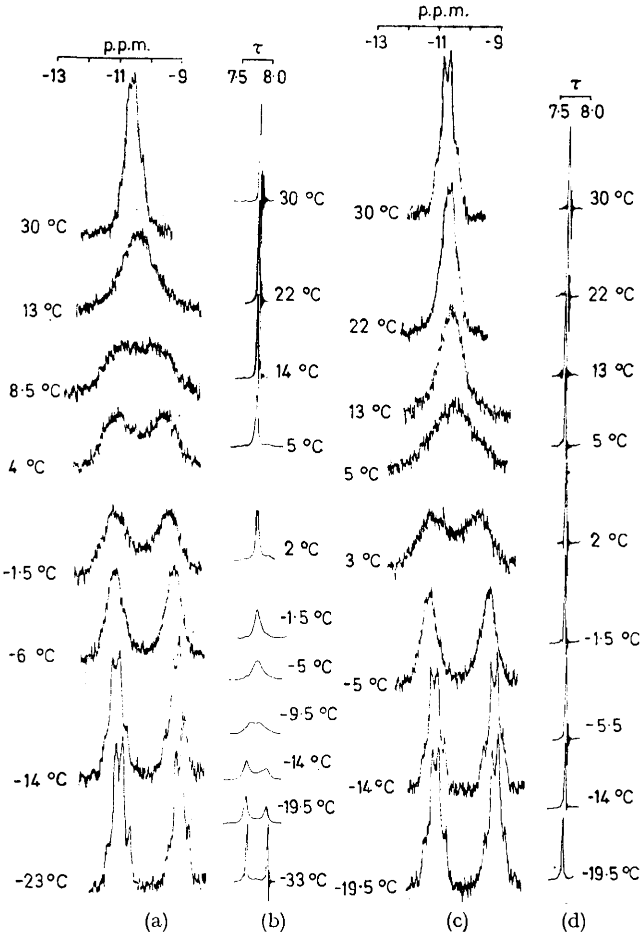

FIGURE 3 N.m.r. spectra of $[RhCl(MeCN)(AsMe_3)_2C_4(CF_3)_4]$, (XIX), in $CDCl_3$ solution. (a) ^{19}F Spectrum of the α-trifluoromethyl groups, MeCN added. (b) ^1H Spectrum of the acetonitrile ligand, MeCN added. (c) Same as (a) but without added MeCN. (d) Same as (b) but without added MeCN

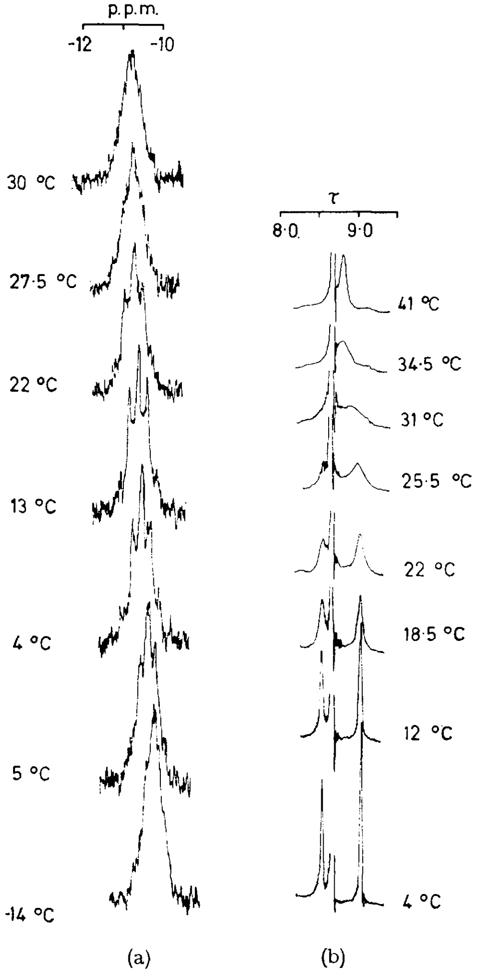

FIGURE 4 N.m.r. spectrum of $[RhCl(AsMe_3)_3C_4(CF_3)_4]$, (XX), in $CDCl_3$ solution. (a) ^{19}F Spectrum of the α-trifluoromethyl groups, Me_3As added. (b) ^1H Spectrum of the arsenic methyl groups, $AsMe_3$ added. The large signal due to the axial arsine ligands is partially omitted for clarity

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* Trimethyl phosphite has a cone angle of 107° while $P(OCH_2)_3CC_2H_5$ would be expected to have a cone angle close to the value of 101° determined for $P(OCH_2)_3CCH_3$.[15] A cone angle of 125° can be estimated for diphenylphospine[16] while trimethylarsine should have a cone angle somewhat less than the angle of 118° reported for trimethylphosphine.[15]

[15] C. A. Tolman, *J. Amer. Chem. Soc.*, 1970, **92**, 2956.

[16] C. A. Tolman, W. C. Seidel, and L. W. Grosser, *J. Amer. Chem. Soc.*, 1974, **96**, 53.

The final series of complexes prepared are the ionic species (XXI)—(XXIII). In a formal sense these complexes can be thought of as derivatives of (X) or its dimethylphenylarsine analogue in which carbon monoxide and the weakly co-ordinated perchlorate are displaced by the ligand L′. It is not certain that these latter species actually exist in solution following treatment of $[RhCl(CO)L_2C_4(CF_3)_4]$ (L = $AsMe_3$ or $AsMe_2Ph$) with $AgClO_4$ in the absence of carbon monoxide since (IX) and (X) can only be obtained in good yield in the presence of an excess of carbon monoxide. However the failure to obtain species such as $[RhL_2C_4(CF_3)_4]X$ (X = ClO_4^- or PF_6^-) (*vide infra*) suggests that one equatorial ligand must be present to prevent decomposition of the metallocycle so it is likely that the carbon monoxide remains co-ordinated after removal of the chlorine. The apparent greater lability of carbon monoxide in $[Rh(CO)(OClO_3)L_2C_4(CF_3)_4]$ (L = $AsMe_3$ or $AsMe_2Ph$) as compared to their chlorine-containing precursors is not surprising considering that in the former the electron density available for π back-bonding is less as evidenced by the high $\nu_{C\equiv O}$ values observed (Table 2). However ligands which are better σ-donors readily co-ordinate giving stable six-co-ordinate ionic complexes as perchlorate salts. The data in Tables 2 and 3 clearly demonstrate the ionic nature of the perchlorate; the complexes behave as normal 1 : 1 electrolytes in acetone solution. The presence of two molecules of acetonitrile in (XXI) is confirmed by the data in Tables 1 and 2 as well as by integration of the ^1H n.m.r. spectrum. No exchange with added acetonitrile occurs at room temperature.

TABLE 3

Conductivity data [a]

Complex	Concentration range ($mol\ l^{-1}$)	Λ_0(Ω^{-1} cm^2 $equiv^{-1}$)
(IX)	$1{\cdot}298 \times 10^{-3}$—$1{\cdot}54 \times 10^{-2}$	108·7
(X)	$1{\cdot}880 \times 10^{-3}$—$1{\cdot}238 \times 10^{-2}$	110·0
(XXI)	$1{\cdot}858 \times 10^{-3}$—$2{\cdot}095 \times 10^{-2}$	120·9
(XXII)	$2{\cdot}067 \times 10^{-3}$—$1{\cdot}399 \times 10^{-2}$	141·7
(XXIII)	$2{\cdot}088 \times 10^{-3}$—$1{\cdot}799 \times 10^{-2}$	135·0

[a] Acetone solution.

The presence of two trimethyl phosphite ligands in (XXII) is shown by the analytical data as well as by integration of the ^1H n.m.r. spectrum. In addition the resonance due to the phosphite methyl groups has changed from the sharp doublet observed for (XXII) to a more complex signal consisting of two sharp outer lines separated by 10·8 Hz and a broad central peak having several shoulders which evidently arises from the overlap of a number of closely spaced lines. The spectrum resembles that found for *cis*-$[Pt(NCO)_2\{P(OMe)_3\}_2]$ [17] and while the lack of resolution of the central lines makes it impossible to obtain a reliable value for $^2J_{PP}$, based on previous results it is likely to be in excess of 20 Hz.[17,18] The ^{19}F n.m.r. spectra of all three complexes are as expected for a six-co-ordinate complex with two identical equatorial ligands.

We have also extended the previously reported [1] n.m.r. studies of $[RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4]$ and find that its behaviour in solution is analogous to that of the labile complexes (XVII)—(XIX). Thus in $CDCl_3$ solution at 31 °C, a sharp singlet is observed at τ 8·20 which can be assigned to water. On cooling to −50 °C this signal shifts to τ 6·64 and broadens markedly so that at −59 °C it has become so broad as to be undetectable. Over this same temperature range, only one signal is observed for the α-CF_3 groups although at the lowest temperature it appears to have begun to broaden. In CH_2Cl_2 solution two resonances could be observed for the α-CF_3 groups at −68 °C showing that a static six-co-ordinate structure had been achieved. These spectra were however of limited quality due to the low solubility of the complex at these temperatures. The marked downfield shift of the water signal at low temperature suggests that at room temperature the equilibrium (1) lies well towards the right

$$[RhCl(H_2O)(AsMe_3)_2C_4(CF_3)_4] \rightleftharpoons [RhCl(AsMe_3)_2C_4(CF_3)_4] + H_2O \quad (1)$$

but shifts to the left on cooling. This is also suggested by the fact that at room temperature the solution has a noticeable yellow colour similar to that of $[RhCl(AsMe_3)_2C_4(CF_3)_4]$ but at the lowest temperatures it has the pale pink colour of the solid complex. That complete dissociation has not occurred at 31 °C is indicated by the fact that the water signal is downfield from free water in this solvent (τ 8·47). The failure to observe separate signals for free and co-ordinated water indicates that at the higher temperature rapid water exchange occurs.

DISCUSSION

It appears from this work that the bis(tertiary arsine)-rhodatetrakis(trifluoromethyl)cyclopentadiene moiety is stable under mild conditions when at least one equatorial ligand is present. This also is the case at least for $[RhCl(AsPh_3)_2C_4(CF_3)_4]$ when it is subjected to cyclotrimerization conditions but in the absence of hexafluorobut-2-yne (150 °C, 2 h, benzene solution, 95% recovery of unchanged complex).[2] However decomposition can occur in the absence of equatorial ligands. Thus reaction of $[RhCl(AsPh_3)_2C_4(CF_3)_4]$ with an equimolar amount of $AgPF_6$ in benzene–ethanol gives an immediate precipitate of a dark brown, flocculent, solid and from the yellow filtrate a tan solid can be isolated whose i.r. spectrum shows the presence of $AsPh_3$ and PF_6^- but from which the strong C–F absorptions of the rhodacycle are absent. This contrasts with the reaction with $AgNO_3$ under identical conditions where AgCl slowly precipitates and $[Rh(NO_3)(AsPh_3)_2C_4(CF_3)_4]$ is formed and with the reaction with $AgPF_6$ in acetonitrile. Again, AgCl slowly precipitates and a complex is obtained which appears from its i.r. spectrum to be $[Rh(MeCN)_2(AsPh_3)_2C_4(CF_3)_4][PF_6]$.

While the rhodacycle can bind a variety of equatorial ligands we have yet to obtain definite evidence that it can bind an acetylene molecule which would be necessary were cyclotrimerization to occur *via* a co-ordination–insertion sequence with the rhodacycle as an intermediate. The ^{19}F n.m.r. spectrum of a benzene solution of $[RhCl(AsMe_3)_2C_4(CF_3)_4]$ containing excess hexafluorobut-2-yne initially shows two weak multiplet signals in

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[17] M. J. Church and M. J. Mays, *J. Inorg. Nuclear Chem.*, 1971, **33**, 253.

[18] D. A. Duddell, J. C. Evans, P. L. Goggin, R. J. Goodfellow, A. J. Rest, and J. G. Smith, *J. Chem. Soc.* (*A*), 1969, **2134**.

addition to the resonances of the metallocycle which might be due to a co-ordinated hexafluorobut-2-yne molecule but the spectrum was not of sufficient quality to enable a good analysis to be made. With time, polymerization of the acetylene occurred and the solution set to a gel. This result was unexpected and at present we have no explanation for it. Clearly more work is necessary to clarify this aspect of the problem.

The variable-temperature n.m.r. spectra of complexes (XVI)—(XIX) shown in Figures 1—3 warrant additional comment. For (XVIII), the chemical-shift difference between the resonances observed for free and bound equatorial ligand at the low temperature limit when added ligand is present is relatively small (0·5 p.p.m.) and comparable to the difference in chemical shift for the non-equivalent arsenic methyl groups. Both sets of signals coalesce at approximately the same temperature and the same coalescence temperature is observed for the arsenic methyl-group resonances in the absence of free ligand. Similar behaviour is observed for (XVII). These observations indicate that the process which leads to averaging of the arsenic methyl groups is the exchange of the equatorial ligand rather than dissociation to the five-co-ordinate metallocycle. Some of the evidence for a small degree of dissociation has been discussed in the preceeding section and this is further supported by the fact that the single arsenic methyl-group resonance in $[RhCl(AsMe_2Ph)_2C_4(CF_3)_4]$ occurs at τ 8·30 at 30 °C while the averaged signal in (XVII) and (XVIII) occurs at τ 8·37 at 30 °C. In each of the complexes (XVII)—(XIX), the coalescence of the α-CF_3 group resonances occurs at a temperature about 15 °C higher than that observed for the corresponding ligand resonances. For each complex this temperature is the same in the absence of added ligand. It is very unlikely that there is a process other than equatorial ligand exchange which leads to the averaging of these latter signals and the difference observed between the ^1H and ^{19}F spectra is most likely due to the considerably greater chemical shift differences between the ^{19}F resonances as compared to the ^1H resonances.

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