Journal of Organometallic Chemistry, 81 (1974) 415—422

PREPARATION AND ^{19}F NMR SPECTRA OF SOME FLUOROOLEFIN COMPLEXES OF RHODIUM(I)

A.C. JARVIS and R.D.W. KEMMITT

Inorganic Research Laboratories, The University, Leicester LE1 7RH (Great Britain)

(Received June 28th, 1974)

Summary

The fluoroolefin complexes $Rh(dpm)(C_2H_4)(CF_2{=}CFX)$, (dpm = dipivaloylmethanato, X = F, CF_3, Cl or Br) have been prepared. Triphenyl-phosphine, -arsine and -stibine displace ethylene from these complexes to give complexes of the type $Rh(dpm)(CF_2{=}CFX)(L)$. ^{19}F NMR studies are consistent with a structure in which the substituent X is in an outside position with respect to the ethylene or ligand L.

Introduction

A number of donor ligands L have been shown to displace ethylene from the complex, $Rh(acac)(C_2H_4)(C_2F_4)$, (acac = $CH_3COCHCOCH_3$) to give complexes of stoichiometry $Rh(acac)(C_2F_4)L_2$, (L = PPh_3, PBu_3, Me_2SO, C_5H_5N; L_2 = $Me_2NCH_2CH_2NMe_2$ and $Ph_2PCH_2CH_2PPh_2$) [1]. We now find that although ethylene is similarly displaced from the dipivaloylmethanato complexes $Rh(dpm)(C_2H_4)$-(fluoroolefin), (dpm = $Me_3CCOCHCOCMe_3$; fluoroolefin = $CF_2{=}CF_2$, $CF_2{=}CFCF_3$, $CF_2{=}CFCl$ or $CF_2{=}CFBr$) by triphenyl-phosphine, -arsine or -stibine, only complexes of stoichiometry Rh(dpm)(fluoroolefin)(L), (L = PPh_3, $AsPh_3$ or $SbPh_3$) are formed.

Herein the preparation and ^{19}F NMR spectra of these complexes is now described. The reactions of some of these complexes with electrophilic acetylenes have been reported [2].

Results and discussion

Treatment of $Rh(dpm)(C_2H_4)_2$ with tetrafluoroethylene in diethyl ether as solvent at room temperature gives a high yield of $Rh(dpm)(C_2H_4)(C_2F_4)$ in a similar manner to that reported for the analogous acetylacetonato compound [1].

TABLE 1

^{19}F NMR CHEMICAL SHIFTS (ppm)[a] FOR THE COMPLEXES Rh(dpm)(L)(CF_2=CFX)

Compound	$\delta(F_1)$	$\delta(F_2)$	$\delta(F_3)$	$\delta(CF_3)$
Rh(dpm)(C_2H_4)(CF_2=CF_2)	34.8			
Rh(dpm)(PPh_3)(CF_2=CF_2)[b]	41.0	49.8		
Rh(dpm)($AsPh_3$)(CF_2=CF_2)[b]	37.0	51.0		
Rh(dpm)($SbPh_3$)(CF_2=CF_2)[b]	27.5	51.2		
Rh(dpm)(C_2H_4)(CF_2=CFCF_3)	36.2	23.0	143.2	2.98
Rh(dpm)(PPh_3)(CF_2=CFCF_3)	32.2	18.5	113.3	1.79
Rh(dpm)($AsPh_3$)(CF_2=CFCF_3)	33.6	13.9	107.2	2.24
Rh(dpm)($SbPh_3$)(CF_2=CFCF_3)	34.8	5.08	95.5	2.38
Rh(dpm)(C_2H_4)(CF_2=CFCl)	39.9	34.6	60.5	
Rh(dpm)(PPh_3)(CF_2=CFCl)	37.7	28.42	44.1	
Rh(dpm)($AsPh_3$)(CF_2=CFCl)[b]	39.4	23.4	39.4	
Rh(dpm)($SbPh_3$)(CF_2=CFCl)	41.7	18.2	31.1	
Rh(dpm)(C_2H_4)(CF_2=CFBr)	37.8	33.2	61.2	
Rh(dpm)(PPh_3)(CF_2=CFBr)	39.9	26.7	35.0	
Rh(dpm)($AsPh_3$)(CF_2=CFBr)[b]	36.4	21.8	36.4	
Rh(dpm)($SbPh_3$)(CF_2=CFBr)	37.2	13.1	26.6	

[a] Measured in CH_2Cl_2 solution relative to internal α,α,α-trifluorotoluene. [b] These complexes all give second order spectra.

The reactions of hexafluoropropene, chlorotrifluoroethylene and bromotrifluoroethylene with Rh(dpm)(C_2H_4)$_2$ similarly give the corresponding fluoroolefin complexes as pale yellow crystalline materials which are very soluble in common organic solvents and are most easily purified by vacuum sublimation. The reaction of triphenylphosphine with Rh(dpm)(C_2H_4)(C_2F_4) in methanol solution at room temperature effects displacement of ethylene from the rhodium to produce the yellow crystalline complex Rh(dpm)(C_2F_4)(PPh_3). Analogous products are formed with triphenylarsine and triphenylstibine. The complexes Rh(dpm)(fluoroolefin)(L), (fluoroolefin = CF_2=CFCF_3, CF_2=CFCl, CF_2=CFBr;

TABLE 2

^{19}F NMR[a] COUPLING CONSTANTS (Hz) FOR COORDINATED AND FREE FLUOROOLEFINS

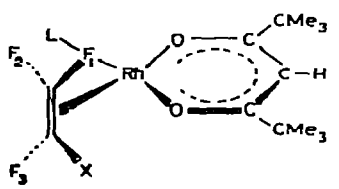
Compound	$J(F_2-F_3)$	$J(F_1-F_3)$	$J(F_1-F_2)$	$J(Rh-F_1)$
Rh(dpm)(C_2H_4)(CF_2=CFCF_3)	12.5	62.6	77.5	
Rh(dpm)(PPh_3)(CF_2=CFCF_3)		64.4	94.6	
Rh(dpm)($AsPh_3$)(CF_2=CFCF_3)	25.6	59.9	89.8	
Rh(dpm)($SbPh_3$)(CF_2=CFCF_3)	30.6	61.2	92.7	
Rh(dpm)(C_2H_4)(CF_2=CFCl)	8.5	62.5	77.0	3.1
Rh(dpm)($AsPh_3$)(CF_2=CFCl)	17.1	59.9	87.5	4.0
Rh(dpm)($SbPh_3$)(CF_2=CFCl)	22.0	63.7	85.9	2.5
Rh(dpm)(C_2H_4)(CF_2=CFBr)	9.2	64.9	75.3	2.7
Rh(dpm)($AsPh_3$)(CF_2=CFBr)	19.9	63.6	87.0	4.2
Rh(dpm)($SbPh_3$)(CF_2=CFBr)	24.0	64.2	89.7	3.1
CF_2=CFCF_3[b]	40.0	120.0	57.0	
CF_2=CFCl[c]	57.0	124.0	75.0	
CF_2=CFBr[c]	58.0	115.0	78.0	

[a] Measured in CH_2Cl_2 solution. [b] Ref. 12. [c] Ref. 11.

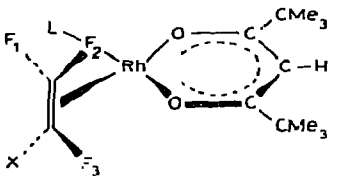
L = PPh_3, $AsPh_3$, $SbPh_3$) may be similarly prepared. The formation of complexes of the type $Rh(dpm)(C_2F_4)(PPh_3)$ should be contrasted with the reaction of the corresponding acetylacetonato complex $Rh(acac)(C_2H_4)(C_2F_4)$, which yields bis-tertiary phosphine complexes $Rh(acac)(C_2F_4)(PR_3)_2$, (R = Ph or Bu) [1]. It would appear that the presence of the bulky tertiary butyl groups present in $Rh(dpm)(C_2F_4)(PPh_3)$ prevents the coordination of a second molecule of triphenylphosphine to the rhodium, since one of the triphenylphosphine ligands present in the bis-phosphine complex would be *cis* to the β-ketoenolate system.

^{19}F NMR spectra

The complexes Rh(dpm)(fluoroolefin)(L) presumably have analogous structures to that of $Rh(acac)(C_2H_4)(C_2F_4)$ which has been the subject of a single crystal X-ray structure determination [3]. The ^{19}F NMR spectra of the complexes (Tables 1 and 2) indicate that the fluoroolefin is rigidly bound to the rhodium and that there is no rotation or oscillation of the fluoroolefin ligand. The complexes can therefore exist in two forms, Ia and Ib, depending on whether the X substituent lies in an "inside" or "outside" position with respect to the ligand L. Further, since the carbon atom attached to the substituent X in the free fluoroolefin becomes asymmetric upon formation of the rhodium complexes there will be optical isomers of the two forms, Ia and Ib.



(Ia)



(Ib)

^{19}F NMR studies on the complex $Rh(\pi\text{-}C_5H_5)(C_2H_4)(CH_2{=}CHF)$ [4] have shown that this complex also exists in two geometric forms depending on the

$J(Rh-F_2)$	$J(Rh-F_3)$	$J(P-F_1)$	$J(P-F_2)$	$J(P-F_3)$	$J(CF_3-F_1)$	$J(CF_3-F_2)$	$J(CF_3-F_3)$
					12.8	7.1	9.7
					14.9		
1.4					14.3	8.6	14.1
1.4					14.3	9.7	
8.6	8.6						
11.4	11.6	6.1	39.3	42.7			
11.3	10.0						
9.2	10.6						
11.2	11.4	5.7	35.7	44.2			
11.4	9.7						

relative orientation of the fluorine atom to the C_2H_4 ligand. These can be distinguished by the relative magnitude of the rhodium—fluorine coupling constants which is larger for the "inside" fluorine [4]. The ^{19}F NMR spectrum of the complex Rh(dpm)(C_2H_4)(CF_2=CFCl) exhibits three fluorine resonances. One of the fluorine resonances has a rhodium—fluorine coupling constant of 3.1 Hz whilst the other two each have J(Rh—F) values of 8.6 Hz. On the basis of previous studies [4] the fluorine with the lower value of J(Rh—F) can therefore be placed in an "outside" position as shown in Ia. Similarly, the ^{19}F NMR spectra of the complexes Rh(dpm)(CF_2=CFX)(L) may also be interpreted in terms of structure Ia or its mirror image. It is apparent from these studies that the displacement of ethylene from Rh(dpm)(C_2H_4)$_2$ by the fluoroolefins occurs by a mechanism which places the X substituent in an "outside" position. Furthermore in the displacement of ethylene from Rh(dpm)(C_2H_4)(CF_2=CFX) by triphenyl-phosphine, -arsine or -stibine there appears to be no change in the orientation of the fluoroolefin with respect to the incoming and outgoing ligands. If the alkene ligands in these complexes are assumed to occupy only one coordinating position, these substitution reactions may proceed via trigonal bipyramidal transition states in which the entering and leaving groups occupy similar positions, as has been proposed in amine substitution reactions of square planar platinum(II) complexes [5]. The complexes studied in our work do not exhibit optical activity. However, since there is no reason to assume preference for one optical isomer over that of the other, the isolation of the complexes as racemic mixtures is to be expected. The preference for the "outside" isomer may be a consequence of steric effects.

While the ^{19}F NMR spectra of the complexes Rh(dpm)(C_2H_4)(CF_2=CFX) clearly indicate that the fluoroolefin is rigid on the NMR time scale the ^{19}F NMR spectra of the tetrafluoroethylene complex, Rh(dpm)(C_2H_4)(C_2F_4) exhibits only one fluorine resonance with rhodium coupling, which is temperature independent from 25 to —90°. In the complex Rh(acac)(C_2H_4)(C_2F_4) the fluorine atoms have also been observed to absorb in one region of the ^{19}F NMR spectrum. Whilst this result has been interpreted [6] in terms of rotation of the tetrafluoroethylene about the metal—tetrafluoroethylene band the observation that the ^{19}F NMR spectra of Rh(dpm)(C_2H_4)(C_2F_4) does not change from 25 to —90° is more in agreement with a rigid structure. This complex is under further investigation. The ^{19}F NMR spectra of the tetrafluoroethylene complexes, Rh(dpm)(C_2F_4)(L), (L = $AsPh_3$ or $SbPh_3$) are all complex and similar in appearance to Rh(π-C_5H_5)(C_2H_4)(C_2F_4) which is of the AA'BB'X type [7].

A comparison of the F—F coupling constants of free and coordinated fluoro-olefins shows a decrease in the size of the vicinal $J(F_2F_3)$ and $J(F_1F_3)$ coupling and a corresponding increase in the magnitude of the geminal coupling $J(F_1F_2)$ [7-11]. These changes have been interpreted in terms of a change of hybridisation of the olefinic carbon atoms from sp^2 to sp^3 hybridisation. Similar trends are observed in the present rhodium(I) complexes although the changes are not as large as have previously been observed in formally zerovalent complexes involving the iron and nickel triads, in which presumably there would be more back-bonding. Replacement of ethylene by triphenyl-phosphine, -arsine, or -stibine ligands in the complexes Rh(dpm)(L)(C_2F_3X) has little effect on the geminal coupling constant but significantly increases the vicinal coupling, $J(F_2F_3)$.

TABLE 3

ANALYTICAL AND OTHER DATA FOR THE COMPLEXES Rh(dpm)(L)(CF_2=CFX)

Compound	Colour	M.p. (°C)[a]	Yield (%)	Analysis, found (calcd.) (%)			Mol. wt. Found[b] (calcd.)
				C	H	F	
Rh(dpm)(C_2H_4)(CF_2=CF_2)	Pale yellow	149 (dec)	87	43.3 (43.6)	5.7 (5.6)	18.6 (18.4)	409 (414)
Rh(dpm)(C_2H_4)(CF_2=CFCF_3)	Yellow	71	86	41.4 (41.2)	4.9 (5.0)	24.8 (24.7)	444 (464)
Rh(dpm)(C_2H_4)(CF_2=CFCl)	Yellow	132 (dec)	81	42.2 (42.0)	5.1 (5.1)	13.1 (13.3)	402 (430)
Rh(dpm)(C_2H_4)(CF_2=CFBr)	Yellow	118 (dec)	88	38.1 (38.0)	4.8 (4.8)	12.2 (12.0)	460 (475)
Rh(dpm)(PPh_3)(CF_2=CF_2)	Pale yellow	195 (dec)	66	56.8 (57.3)	5.3 (5.3)	11.6 (11.7)	676 (648)
Rh(dpm)($AsPh_3$)(CF_2=CF_2)	Pale yellow	189 (dec)	78	53.6 (53.9)	4.9 (4.9)	11.1 (11.0)	726 (692)
Rh(dpm)($SbPh_3$)(CF_2=CF_2)	Pale yellow	154 (dec)	80	50.4 (50.3)	4.6 (4.6)	10.0 (10.3)	728 (738)
Rh(dpm)(PPh_3)(CF_2=CFCF_3)	Pale yellow	176 (dec)	67	54.8 (55.1)	4.9 (4.9)	16.3 (16.3)	681 (698)
Rh(dpm)($AsPh_3$)(CF_2=CFCF_3)	Pale yellow	154 (dec)	87	51.9 (51.9)	4.6 (4.6)	15.1 (15.4)	724 (742)
Rh(dpm)($SbPh_3$)(CF_2=CFCF_3)	Yellow	162 (dec)	81	48.7 (48.6)	4.4 (4.3)	14.4 (14.4)	766 (788)
Rh(dpm)(PPh_3)(CF_2=CFCl)	Pale yellow	188 (dec)	81	56.1 (56.0)	5.1 (5.0)	8.9 (8.6)	661 (664)
Rh(dpm)($AsPh_3$)(CF_2=CFCl)	Pale yellow	187 (dec)	88	52.5 (52.5)	4.9 (4.8)	7.8 (8.0)	691 (708)
Rh(dpm)($SbPh_3$)(CF_2=CFCl)	Yellow	154 (dec)	80	49.1 (49.3)	4.6 (4.5)	7.3 (7.5)	747 (754)
Rh(dpm)(PPh_3)(CF_2=CFBr)	Light brown	169 (dec)	76	52.1 (52.4)	4.7 (4.8)	7.9 (8.1)	694 (709)
Rh(dpm)($AsPh_3$)(CF_2=CFBr)	Light brown	147 (dec)	88	49.0 (49.3)	4.2 (4.5)	7.7 (7.5)	732 (753)
Rh(dpm)($SbPh_3$)(CF_2=CFBr)	Light brown	153 (dec)	85	46.6 (46.8)	4.3 (4.3)	6.8 (7.2)	760 (799)

[a] Uncorrected. [b] Molecular weights were determined osmometrically in chloroform.

Experimental

Analytical data, yields and melting points for all new complexes are given in Table 3. Proton NMR spectra (Table 4) were recorded at 60 MHz on a Varian Associates T60 spectrometer. IR spectra (Table 5) were recorded on a Perkin—Elmer model 225 spectrophotometer. Fluorine NMR spectra were recorded at 94.1 MHz on a JEOL JNM-PS-100 spectrometer.

$Rh(dpm)(C_2H_4)_2$ was prepared in diethyl ether solution by reaction of $[RhCl(C_2H_4)_2]_2$ with $(CH_3)_3CCOCH_2COC(CH_3)_3$ in the presence of aqueous KOH [2].

Preparation of the complexes $Rh(dpm)(C_2H_4)(CF_2{=}CFX)$

A solution of $Rh(dpm)(C_2H_4)_2$ in diethyl ether was introduced into a Carius tube (150 ml). An excess of the appropriate fluoroolefin was condensed onto the solution at —196°, and the tube sealed under vacuum. After shaking at room temperature for 30 min, the tube was opened and the solution evaporated to dryness under reduced pressure. Sublimation of the residue gave the appropriate fluoroolefin complex as pale yellow crystals.

Preparation of the complexes $Rh(dpm)(L)(CF_2{=}CFX)$

Triphenyl-phosphine, -arsine or -stibine (ca. 1.0 mmol) was added to a solution of the appropriate fluoroolefin complex (1.0 mmol) in methanol solution (10 ml). After vigorous stirring for 20 min, the precipitated complex was filtered off and recrystallised from CH_2Cl_2/methanol solution.

TABLE 4

^1H NMR[a] SPECTRA FOR THE COMPLEXES $Rh(dpm)(L)(CF_2{=}CFX)$

Complex	Phenyl (15H)	3-CH (1H)	t-butyl (9H)	t-butyl (9H)	Olefinic (4H)
$Rh(dpm)(C_2H_4)(CF_2{=}CF_2)$		4.17s	8.88s	8.90s	5.88(br)
$Rh(dpm)(PPh_3)(CF_2{=}CF_2)$[b]	2.56m	4.34s	8.84s	9.43s	
$Rh(dpm)(AsPh_3)(CF_2{=}CF_2)$	2.52m	4.20s	8.88s	9.40s	
$Rh(dpm)(SbPh_3)(CF_2{=}CF_2)$	2.55m	4.17s	8.88s	9.23s	
$Rh(dpm)(C_2H_4)(CF_2{=}CFCF_3)$		4.10s	8.89s (br)[c]		5.69(br)
$Rh(dpm)(PPh_3)(CF_2{=}CFCF_3)$[b]	2.60m	4.28s	8.89s	9.53s	
$Rh(dpm)(AsPh_3)(CF_2{=}CFCF_3)$	2.54m	4.17s	8.88s	9.43s	
$Rh(pdm)(SbPh_3)(CF_2{=}CFCF_3)$	2.55m	4.12s	8.84s	9.31s	
$Rh(dpm)(C_2H_4)(CF_2{=}CFCl)$		4.17s	8.87s	8.91s	4.82(br)
$Rh(dpm)(PPh_3)(CF_2{=}CFCl)$[b]	2.53m	3.89s	8.84s	9.50s	
$Rh(dpm)(AsPh_3)(CF_2{=}CFCl)$	2.51m	4.25s	8.84s	9.40s	
$Rh(dpm)(SbPh_3)(CF_2{=}CFCl)$	2.54m	4.18s	8.86s	9.38s	
$Rh(dpm)(C_2H_4)(CF_2{=}CFBr)$		4.38s	8.87s	8.92s	5.95(br)
$Rh(dpm)(PPh_3)(CF_2{=}CFBr)$[b]	2.44m	4.25s	8.84s	9.50s	
$Rh(dpm)(AsPh_3)(CF_2{=}CFBr)$	2.68m	4.45s	8.85s	9.46s	
$Rh(dpm)(SbPh_3)(CF_2{=}CFBr)$	2.85m	4.40s	8.85s	9.28s	

[a] Measured in $CDCl_3$ solution at room temperature; chemical shifts (τ) are relative to internal TMS. [b] Spectra obtained at 0°. [c] Integrates as 18H.

TABLE 5

SELECTED INFRARED ABSORPTIONS[a] FOR THE COMPLEXES Rh(dpm)(L)(CF_2=CFX)

Compound	dpm	C—F	Others
Rh(dpm)(C_2H_4)(CF_2=CF_2)	1553, 1541, 1502	1182, 1161, 1148, 1054	999, 882, 810, 782, 749, 728
Rh(dpm)(PPh_3)(CF_2=CF_2)	1553, 1539, 1506	1181, 1141, 1099, 1049	798, 756, 744, 692
Rh(dpm)($AsPh_3$)(CF_2=CF_2)	1555, 1541, 1508	1186, 1144, 1129, 1084	809, 794, 747, 740, 699
Rh(dpm)($SbPh_3$)(CF_2=CF_2)	1562, 1551, 1529	1221, 1194, 1159, 1131	814, 796, 760, 734, 698
Rh(dpm)(C_2H_4)(CF_2=$CFCF_3$)	1546, 1502	1199, 1180, 1142, 1124	982, 972, 880, 812, 776, 746, 691
Rh(dpm)(PPh_3)(CF_2=$CFCF_3$)	1549, 1540, 1503	1198, 1181, 1142, 1122	971, 880, 778, 759, 747, 696
Rh(dpm)($AsPh_3$)(CF_2=$CFCF_3$)	1547, 1539, 1504	1199, 1181, 1144, 1118	971, 879, 784, 756, 742, 691
Rh(dpm)($SbPh_3$)(CF_2=$CFCF_3$)	1548, 1540, 1506	1198, 1181, 1144, 1123	969, 882, 780, 754, 740, 692
Rh(dpm)(C_2H_4)(CF_2=CFCl)	1552, 1536, 1501	1243, 1222, 1178, 1142	932, 876, 801, 713
Rh(dpm)(PPh_3)(CF_2=CFCl)	1553, 1537, 1503	1242, 1220, 1179, 1137	928, 880, 801, 743, 737, 723, 701, 692
Rh(dpm)($AsPh_3$)(CF_2=CFCl)	1549, 1534, 1504	1242, 1219, 1179, 1141	936, 889, 803, 741, 737, 723, 691
Rh(dpm)($SbPh_3$)(CF_2=CFCl)	1552, 1537, 1501	1242, 1221, 1181, 1142	932, 881, 803, 744, 733, 724, 697
Rh(dpm)(C_2H_4)(CF_2=CFBr)	1552, 1536, 1503	1239, 1217, 1162	879, 814, 716
Rh(dpm)(PPh_3)(CF_2=CFBr)	1552, 1536, 1502	1238, 1216, 1134	873, 794, 746, 737, 718, 684
Rh(dpm)($AsPh_3$)(CF_2=CFBr)	1553, 1538, 1507	1242, 1218, 1177, 1138	876, 800, 768, 736, 720, 690
Rh(dpm)($SbPh_3$)(CF_2=CFBr)	1551, 1538, 1506	1240, 1219, 1178, 1139	878, 800, 769, 730, 719, 691

[a] All IR spectra in cm^{-1} as Nujol mulls.

Acknowledgement

We thank Johnson Matthey for a generous loan of hydrated rhodium trichloride, Mrs. Sheila Davies for running the ^{19}F NMR spectra, and the S.R.C. for a grant (to A.C.J.).

References

1 G.W. Parshall and F.N. Jones, J. Amer. Chem. Soc., 87 (1965) 5356.
2 A.C. Jarvis and R.D.W. Kemmitt, in press.
3 J.A. Evans and D.R. Russell, Chem. Commun., (1971) 197.
4 G.S. Reddy and R. Cramer, Inorg. Chem., 12 (1973) 346.
5 A.L. Odell and H.A. Raethel, Chem. Commun., (1969) 87.
6 F.R. Hartley, Angew. Chem., Int. Ed. Engl., 11 (1972) 596.
7 R. Cramer, J.B. Kline and J.D. Roberts, J. Amer. Chem. Soc., 91 (1969) 2519.
8 R. Burt, M. Cooke and M. Green, J. Chem. Soc. A, (1970) 2975.
9 C.S. Cundy, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1970) 1647.
10 M. Green, R.B.L. Osborn, A.J. Rest and F.G.A. Stone, J. Chem. Soc. A, (1968) 2525.
11 R. Fields, M.M. Germain, R.N. Haszeldine and P.W. Wiggans, J. Chem. Soc. A, (1970) 1969.
12 E. Pitcher and F.G.A. Stone, Spectrochim. Acta, 17 (1961) 1244.