Ruthenium Complexes containing Group 5B Donor Ligands. Part 4.[1] Synthesis, Crystal and Molecular Structure of *def*-Tri-μ-chloro-*h*-diphenylphosphinito-*bgi*-tris(diphenylphosphinous acid)-*ac*-bis(methyl diphenylphosphinite)diruthenium(II)

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Pyrolysis of solutions containing $[\{P(OMe)Ph_2\}_3RuCl_3Ru\{P(OMe)Ph_2\}_3]Cl$ for 12 h at 120 °C gives yellow crystals (1) shown by *X*-ray diffraction analysis to be $[\{P(OMe)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{P(OH)Ph_2\}_2(Ph_2PO)]$. The crystals are monoclinic, space group $P2_1/c$ with a = 13.19, b = 21.98, c = 24.98 Å, β = 109.40°, and contain one molecule per asymmetric unit. The structure was solved using 1 534 film data, and refined to R 0.11.

Related pyrolysis reactions give the compounds $[\{P(OEt)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{P(OH)Ph_2\}_2(Ph_2PO)]$ (2) and $[\{P(OEt)Ph_2\}_2\{P(OH)Ph_2\}RuBr_3Ru\{P(OH)Ph_2\}_2(Ph_2PO)]$ (3).

IN recent years, a number of ruthenium(II) complexes containing tertiary phosphinites $P(OR)R_2$ [1] and phosphonites $P(OR)_2R^1$ have been synthesised. These include compounds such as $[RuH_2\{P(OEt)_2Ph\}_4]$,[2] $[RuCl_2\{P(OMe)_2Ph\}_4]$,[3] $[RuCl_2\{P(OR)Ph_2\}_3]$ (R = Me, Et),[3] $[RuH\{P(OR)_2Ph\}_5]X$ (R = Me, Et; X = $[PF_6]^-$;[4] R = Me, X = $[BPh_4]^-$ [5,6]), $[Ru\{P(OMe)_2Ph\}_6][BPh_4]_2$,[6] and $[L_3RuX_3RuL_3][BPh_4]$ [L = $P(OMe)_2Ph$, $P(OMe)Ph_2$, X = Cl; L = $P(OEt)_2Ph$, $P(OEt)Ph_2$; X = Cl, Br].[6]

However, unlike the related tertiary phosphines, no neutral dimeric or anionic complexes of type $[L_3RuX_3RuXL_2]$ or $[L_3RuX_3RuL_3][RuX_3L_3]$ [L = $P(OR)R_2{}^1$ or $P(OR)_2R^1$] are known † and therefore, the aim of this present work was an attempt to synthesise such compounds.

RESULTS

Several years ago, Prince and Raspin [8] demonstrated that the pyrolysis products of $[(PEt_2Ph)_3RuCl_3Ru(PEt_2Ph)_3]Cl$ were dependent upon the solvent media and the temperature of pyrolysis. Thus, in propyl propionate at 60 or 120 °C or methyl acetate at 120 °C, $[(PEt_2Ph)_3RuCl_3RuCl(PEt_2Ph)_2]$ was formed [9] whereas in methyl acetate at 60 °C, $[Ru_2Cl_3(PEt_2Ph)_6][RuCl_3(PEt_2Ph)_3]$ [10] was produced.

Thus, by analogy with that work, the yellow solution obtained from the reaction of $[\{RuCl_2(C_7H_8)\}_n]$ and $P(OMe)Ph_2$ in methanol, which contains $[\{P(OMe)Ph_2\}_3RuCl_3Ru\{P(OMe)Ph_2\}_3]Cl$,[6] was reduced in volume and then pyrolysed at 120 °C for 12 h. The resulting bright yellow crystalline solid (1) was shown by e.s.r. and magnetic measurements to be diamagnetic and the far-infrared spectrum (400—200 cm^{-1}) was very similar to $[\{P(OMe)Ph_2\}_3RuCl_3Ru\{P(OMe)Ph_2\}_3][BPh_4]$, containing only a broad band at 260 cm^{-1}, indicating that (1) probably contains a triple chloride bridge but *no* terminal chlorides. However, the infrared spectrum (4 000—400 cm^{-1}) revealed extra features not present in the spectrum of the ionic dimer, *e.g.* a broad band at 3 250 cm^{-1} and strong bands at 1 090, 920 and 855 cm^{-1}, suggesting the presence of Ph_2POH and Ph_2PO^- groups [11] in addition to $P(OMe)Ph_2$. The same compound was obtained if the pyrolysis reaction was carried out at 60 °C. Although a full elemental analysis of (1) was obtained, the compound was too insoluble and involatile for n.m.r. or mass spectroscopy, or molecular weight studies. Therefore, an *X*-ray structural determination of (1) was undertaken, the results of which are described below. Final parameters are in Table 1. Structure-factor tables are deposited as Supplementary Publication No. SUP 21929 (5 pp., 1 microfiche).‡ Selected bond lengths are given in Table 2, and mean values of chemically equivalent angles in Table 3. A view of the molecule, showing only one atom for each phenyl ring, is given in Figure 1.

DISCUSSION

Unlike the expected neutral dimer $[\{P(OMe)Ph_2\}_3RuCl_3RuCl\{P(OMe)Ph_2\}_2]$, (1) contains two methyl diphenylphosphinite groups and four other oxyphosphorus ligands. The diamagnetism of the compound and the long Ru ··· Ru distance (3.425 Å), which indicate no direct metal–metal interaction,[12] suggest a ruthenium(II) complex. One half of the dimer contains both methoxy-groups and interatomic distances suggest that a proton on O(1) interacts primarily with O(5). In the other half-molecule, there must *formally* be one Ph_2PO^- group and two Ph_2POH groups. The most plausible

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† The diamagnetic complexes $[Ru_2Cl_3L_6][RuCl_4L_2]$ [L = $P(OEt)_3$, $P(OMe)Ph_2$, $P(OEt)_2Ph$] have been synthesised by direct reaction of $RuCl_3$ with L.[7] However, as written, these contain paramagnetic ruthenium(III) anions and therefore, it is more likely that they should be reformulated as $[Ru_2Cl_3L_6]Cl$ or even $[Ru_2Cl_3L_6][RuCl_3L_3]$ complexes.

‡ For details see Notices to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

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arrangement is to place protons on O(2) and O(4), both of which interact with a negative charge on O(3). In two compounds, similar arrangements of atoms have been confirmed by *X*-ray analysis, and others probably exist[13-16] [Figures 2 (ref. 15) and 3 (ref. 16)].

Pyrolysis of the yellow solution obtained from the reaction of $[\{RuCl_2(C_7H_8)\}_n]$ and $P(OEt)Ph_2$ in ethanol also gave an insoluble, crystalline yellow solid (2) whose infrared spectrum contained all the additional features found for (1) [plus bands characteristic of $P(OEt)Ph_2$], and which analysed very well for $[\{P(OEt)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{P(OH)Ph_2\}_2(Ph_2PO)]$. The same compound (2) was also obtained if $PClPh_2$ is refluxed with $[RuCl_2(PPh_3)_3]$ in aqueous ethanol whereas in hexane, earlier studies[17] showed that $[(PClPh_2)_3RuCl_3RuCl(PClPh_2)_2]$ is formed. Crystals of (2) are orthorhombic, $a = 26.01$, $b = 43.79$, $c = 24.56$ Å, space group *Fddd* (No. 70). Photographs indicate a substantially disordered structure, and the calculated density (1.50 g cm^{-3}) indicates

TABLE 1

Fractional co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^3$/Å^2) for (1). Mean estimated standard deviations are Ru, 0.004; Cl, 0.012; P, 0.015; O, 0.04; C(methyl), 0.07; and ring centres, 0.03 Å

Atom	*x*	*y*	*z*	*U*
Ru(1)	1 796	2 568	3 295	*
Ru(2)	2 169	2 546	4 718	*
Cl(1)	2 762	1 885	4 074	*
Cl(2)	2 611	3 301	4 077	*
Cl(3)	560	2 521	3 851	*
P(1)	940	1 790	2 737	69
P(2)	3 060	2 612	2 858	62
P(3)	865	3 269	2 686	40
P(4)	3 705	2 658	5 431	49
P(5)	1 342	3 199	5 145	59
P(6)	1 744	1 757	5 175	57
O(1)	2 600	2 637	2 214	74
O(2)	3 672	2 576	6 039	145
O(3)	1 905	3 145	5 805	93
O(4)	1 619	1 896	5 758	65
O(5)	1 231	1 732	2 156	70
O(6)	414	3 040	2 061	74
C(1)	4 054	3 238	3 017	86
C(2)	4 612	3 516	3 536	148
C(3)	5 258	4 026	3 549	131
C(4)	5 346	4 256	3 045	150
C(5)	4 787	3 978	2 526	268
C(6)	4 142	3 469	2 513	177
C(7)	4 026	1 967	2 975	112
C(8)	3 984	1 608	2 505	150
C(9)	4 670	1 107	2 572	196
C(10)	5 398	966	3 109	166
C(11)	5 440	1 324	3 576	137
C(12)	4 754	1 825	3 512	105
C(13)	−534	1 770	2 474	44
C(14)	−1 080	1 753	2 867	111
C(15)	−2 204	1 779	2 680	132
C(16)	−2 782	1 819	2 099	126
C(17)	−2 235	1 835	1 705	226
C(18)	−1 111	1 810	1 892	115
C(19)	1 304	1 017	3 009	84
C(20)	2 367	818	3 146	60
C(21)	2 650	232	3 361	86
C(22)	1 869	−156	3 439	133
C(23)	804	43	3 302	184
C(24)	522	630	3 086	137
C(25)	−292	3 624	2 814	107
C(26)	−1 178	3 233	2 697	109
C(27)	−2 119	3 431	2 784	223
C(28)	−2 174	4 019	2 990	175
C(29)	−1 289	4 409	3 106	193
C(30)	−347	4 211	3 018	208
C(31)	1 610	3 981	2 627	49
C(32)	1 989	4 418	3054	118
C(33)	2 432	4 961	2 942	122
C(34)	2 495	5 068	2 401	78
C(35)	2 115	4 632	1 973	178
C(36)	1 673	4 088	2 086	115
C(37)	4 462	3 350	5 464	38
C(38)	5 042	3 531	5 119	108
C(39)	5 590	4 087	5 208	209
C(40)	5 558	4 462	5 655	107
C(41)	4 978	4 281	6 007	155
C(42)	4 430	3 725	5 911	143
C(43)	4 840	2 186	5 529	64
C(44)	5 451	1 989	6 074	173
C(45)	6 332	1 603	6 146	205
C(46)	6 602	1 416	5 675	108
C(47)	5 990	1 613	5 131	231
C(48)	5 110	1 999	5 058	103
C(49)	1 540	4 040	4 983	50
C(50)	1 170	4 319	4 450	296
C(51)	1 244	4 952	4 406	236
C(52)	1 689	5 304	4 894	174
C(53)	2 058	5 024	5 428	233
C(54)	1 984	4 392	5 473	279
C(55)	−44	3 098	5 050	40
C(56)	−437	2 869	5 466	89
C(57)	−1 542	2 778	5 340	121
C(58)	−2 253	2 916	4 798	161
C(59)	−1 860	3 145	4 383	115
C(60)	−755	3 236	4 508	88
C(61)	2 634	1 091	5 325	41
C(62)	3 245	990	5 893	67
C(63)	4 010	522	6 037	110
C(64)	4 161	157	5 611	113
C(65)	3 549	258	5 042	61
C(66)	2 785	726	4 899	59
C(67)	514	1 334	4 894	78
C(68)	−151	1 236	5 220	438
C(69)	−1 080	881	5 004	435
C(70)	−1 343	626	4 462	188
C(71)	−677	725	4 136	346
C(72)	252	1 078	4 352	205
C(73)	−560	3 275	1 618	137
C(74)	1 138	1 189	1 758	129

* Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru(1)	61	27	47	9	18	12
Ru(2)	63	16	45	−1	16	−5
Cl(1)	68	13	52	1	6	−7
Cl(2)	32	27	50	13	27	4
Cl(3)	95	54	44	10	9	−4

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half a molecule per asymmetric unit ($D_c = 1.50$ g cm^{-3} for $Z = 16$), suggesting that the molecules are disordered, about a two-fold axis or centre of symmetry.

Furthermore, if the yellow solution containing the $[\{P(OEt)Ph_2\}_3RuCl_3Ru\{P(OEt)Ph_2\}_3]^+$ cation is treated with an excess of lithium bromide before pyrolysis, the resulting yellow, crystalline solid (3) analyses very well for $[\{P(OEt)Ph_2\}_2\{P(OH)Ph_2\}RuBr_3Ru\{P(OH)Ph_2\}_2(Ph_2PO)]$.

TABLE 2

Selected bond lengths in (1). Estimated standard deviations are: Ru–Cl, 0.015; Ru–P, 0.018; P–O, 0.05; P–C, 0.07; and O–C, 0.09 Å

Ru(1)–Cl(1)	2.454	Ru(2)–Cl(1)	2.478
Ru(1)–Cl(2)	2.484	Ru(2)–Cl(2)	2.507
Ru(1)–Cl(3)	2.471	Ru(2)–Cl(3)	2.478
Ru(1)–P(1)	2.258	Ru(2)–P(4)	2.222
Ru(1)–P(2)	2.277	Ru(2)–P(5)	2.271
Ru(1)–P(3)	2.226	Ru(2)–P(6)	2.248
P(1)–O(5)	1.63	P(4)–O(2)	1.54
P(1)–C(13)	1.83	P(4)–C(37)	1.81
P(1)–C(19)	1.83	P(4)–C(43)	1.77
P(2)–O(1)	1.52	P(5)–O(3)	1.57
P(2)–C(1)	1.85	P(5)–C(49)	1.93
P(2)–C(7)	1.86	P(5)–C(55)	1.78
P(3)–O(6)	1.56	P(6)–O(4)	1.55
P(3)–C(25)	1.83	P(6)–C(61)	1.84
P(3)–C(31)	1.88	P(6)–C(67)	1.80
O(5)–C(74)	1.53		
O(6)–C(73)	1.48		
O(1) ··· O(5)	2.66	O(2) ··· O(3)	2.54
O(1) ··· O(6)	2.92	O(2) ··· O(4)	2.97
O(5) ··· O(6)	3.05	O(3) ··· O(4)	2.77

TABLE 3

(*a*) Selected bond angles in (1). Estimated standard deviations are 0.5° for all angles given

Cl(1)–Ru(1)–Cl(2)	78.3	Cl(1)–Ru(2)–Cl(2)	77.5
Cl(1)–Ru(1)–Cl(3)	78.1	Cl(1)–Ru(2)–Cl(3)	77.5
Cl(1)–Ru(1)–P(1)	92.7	Cl(1)–Ru(2)–P(6)	93.6
Cl(1)–Ru(1)–P(2)	97.8	Cl(1)–Ru(2)–P(4)	100.7
Cl(1)–Ru(1)–P(3)	171.5	Cl(1)–Ru(2)–P(5)	168.3
Cl(2)–Ru(1)–Cl(3)	77.2	Cl(2)–Ru(2)–Cl(3)	76.7
Cl(2)–Ru(1)–P(1)	166.8	Cl(2)–Ru(2)–P(6)	170.4
Cl(2)–Ru(1)–P(2)	98.9	Cl(2)–Ru(2)–P(4)	95.5
Cl(2)–Ru(1)–P(3)	94.9	Cl(2)–Ru(2)–P(5)	97.6
Cl(3)–Ru(1)–P(1)	91.6	Cl(3)–Ru(2)–P(6)	98.1
Cl(3)–Ru(1)–P(2)	174.8	Cl(3)–Ru(2)–P(4)	172.1
Cl(3)–Ru(1)–P(3)	95.5	Cl(3)–Ru(2)–P(5)	91.1
P(1)–Ru(1)–P(2)	91.8	P(6)–Ru(2)–P(4)	89.6
P(1)–Ru(1)–P(3)	93.0	P(6)–Ru(2)–P(5)	90.5
P(2)–Ru(1)–P(3)	88.2	P(4)–Ru(2)–P(5)	90.3
Ru(1)–Cl(1)–Ru(2)	87.9		
Ru(1)–Cl(2)–Ru(2)	86.6		
Ru(1)–Cl(3)–Ru(2)	87.5		

(*b*) Mean values of chemically distinct angles in (1)

Atoms	Angle/°	Number	Estimated standard deviation
Ru–Cl–Ru	87.3	3	0.6
Cl–Ru–Cl	77.6	6	0.5
P–Ru–Cl(*cis*)	95.6	12	3.0
P–Ru–Cl(*trans*)	170.6	6	1.5
P–Ru–P	90.6	6	0.8
Ru–P–O	113.8	6	1.0
Ru–P–C	118.7	12	1.0
O–P–C	101.6	12	1.5
C–P–C	99	6	3
P–O–C	128	2	5

As expected, $[\{P(OR)Ph_2\}_3RuCl_3Ru\{P(OR)Ph_2\}_3][BPh_4]$ (R = Me or Et) was recovered unchanged after pyrolysis. However, for $[\{P(OEt)Ph_2\}_3RuCl_3Ru\{P(OEt)Ph_2\}_3]X$ (X = $[SCN]^-$, $[CN]^-$, or $[S_2PMe_2]^-$), pyrolysis gave yellow solids whose infrared spectra are identical with (2). This suggests that the first step is nucleophilic attack of $[X]^-$ on a co-ordinated alkoxy-group to give a Ph_2PO^- group and RX. This is presumably followed by stepwise hydrolysis of some of the $P(OR)Ph_2$ groups, the partially hydrolysed product then precipitating out because of its insolubility. Attempts to make (1), (2), or (3) undergo further reactions or to synthesise the corresponding phosphonite complexes have proved unsuccessful to date.

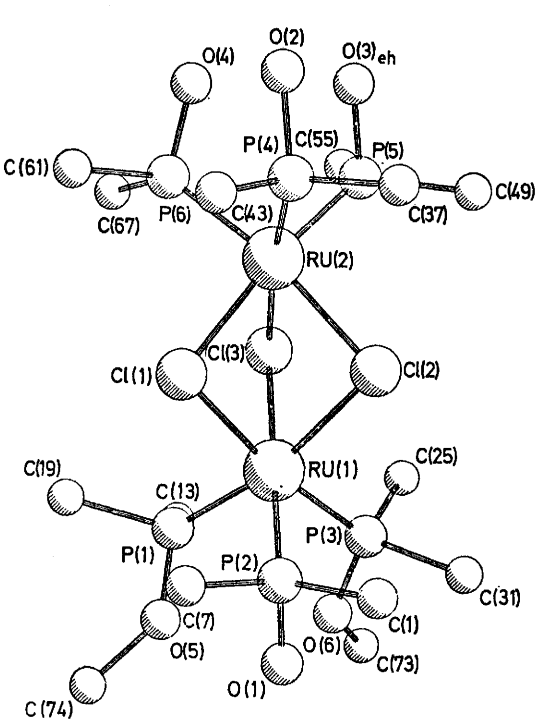

FIGURE 1 Structure of $[\{P(OMe)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{P(OH)Ph_2\}_2(Ph_2PO)]$ (1)

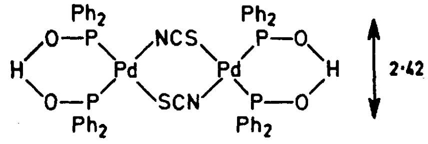

FIGURE 2 Structure of $[(Ph_2PO)_2HPd(SCN)_2Pd(Ph_2PO)_2H]$ (ref. 15)

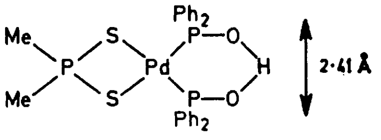

FIGURE 3 Structure of $[Pd(S_2PMe_2)(Ph_2PO)_2H]$ (ref. 16)

EXPERIMENTAL

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4 000—200 cm^{-1} on Perkin-Elmer 225 and 557 grating spectrometers using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Magnetic measurements were made on a Faraday balance. Melting points were determined with a Köfler hot-stage microscope and are uncorrected. Standard crystallographic calculations were performed at the Edinburgh Regional Computing Centre.[18]

Crystal Data.—$C_{74}H_{69}Cl_3O_6P_6Ru_2$, M = 1 549, yellow monoclinic plates, a = 13.19(1), b = 21.98(2), c = 24.98(2) Å, β = 109.4(1)°, U = 6 831 Å^3, D_m = 1.45 g cm^{-3}, Z = 4, D_c = 1.49 g cm^{-3}. Space group $P2_1/c$ (No. 14), Cu-K_α radiation, λ = 1.5418 Å; μ(Cu-K_α) = 65 cm^{-1}.

Structure Determination.—Data were collected from a single crystal, a plate of thickness 0.15 mm and cross-section 0.16 mm^2, using multiple film packs. Data for layers 0—5*kl* were collected by the equi-inclination Weissenberg method, and limited data for layers *hk*0—2 by the precession method. The photographs were of poor quality, and suggested disorder in the crystal. The films were scanned using rotating-drum film scanners, the Weissenberg on an Optronics instrument, and the precession on a Saab. Merging of the data gave 1 534 independent reflections significantly above background.

The positions of two independent ruthenium atoms, both having y *ca.* 0.25, were determined from the Patterson function, and the subsequent difference-Fourier synthesis (R 0.41) had significant pseudo-symmetry. The choice of three positions for chlorine atoms enabled all phosphorus and oxygen atoms to be found in subsequent difference syntheses. The phenyl groups could only be located approximately, and were refined as idealised groups with all C–C bonds 1.40 Å and all C–C–C angles 120°. At this stage the two terminal methyl groups were clearly indicated, but no attempt was made to locate hydrogen atoms. With phenyl groups constrained as above, and anisotropic thermal parameters for Ru and Cl only, the structure was refined treating the parameters in two large blocks, to convergence at R 0.11. Weights were of the form $W = X.Y$ with $X = \sin\theta/0.3$ for $\sin\theta < 0.3$, and 1.0 otherwise, and $Y = 100/|F_o|$ for $|F_o| < 100$ and 1.0 otherwise. A final difference Fourier synthesis did not show any features above one-third the mean height of a carbon atom, and there were broad peaks near the worst determined phenyl rings.

def-*Tri*-μ-*chloro*-h-*diphenylphosphinito*-bgi-*tris*(*diphenylphosphinous acid*)-ac-*bis*(*methyl diphenylphosphinite*)*diruthenium*(II) * (1).—[{(RuCl$_2$(C$_7$H$_8$)}$_n$] [19] (0.22 g) was refluxed with an excess of P(OMe)Ph$_2$ (0.50 ml) in methanol (10 ml) for 4 h under nitrogen to give a yellow solution. The solution was filtered to remove any unchanged starting material and then concentrated to a volume of *ca.* 5 ml. This solution was then pyrolysed in an evacuated, sealed tube at 120 °C for 12 h. The bright yellow crystals formed were filtered off, washed with methanol and diethyl ether, and dried *in vacuo*, m.p. >285 °C (Found: C, 56.6; H, 4.5; Cl, 6.5; P, 13.0; Ru, 11.0. Calc. for $C_{74}H_{69}Cl_3O_6P_6Ru_2$: C, 57.4; H, 4.5; Cl, 6.9; P, 12.0; Ru, 13.0%).

def-*Tri*-μ-*chloro*-h-*diphenylphosphinito*-bgi-*tris*(*diphenylphosphinous acid*)-ac-*bis*(*ethyl diphenylphosphinite*)*diruthenium*(II) (2).—(*a*) Prepared as for (1) by reaction of [{RuCl$_2$(C$_7$H$_8$)}$_n$] and P(OEt)Ph$_2$ in ethanol followed by concentration and pyrolysis at 120 °C for 12 h, m.p. 225 °C (Found: C, 57.3; H, 4.6; Cl, 6.4; P, 11.9. Calc. for $C_{76}H_{73}Cl_3O_6P_6Ru_2$: C, 57.9; H, 4.6; Cl, 6.7; P, 11.8%). (*b*) [RuCl$_2$(PPh$_3$)$_3$] (0.20 g) and PClPh$_2$ (0.50 ml) were refluxed in an ethanol (25 ml)–water (5 ml) mixture. After a few minutes, the solution turned yellow and after 2 h a yellow *solid* had formed, shown by i.r. spectroscopy and m.p. to be identical with (2) (Found: C, 56.6; H, 4.5. Calc. for $C_{76}H_{73}Cl_3O_6P_6Ru_2$: C, 57.9; H, 4.6%). (*c*) [{RuCl$_2$(C$_7$H$_8$)}$_n$] (0.02 g) was refluxed with excess of P(OEt)Ph$_2$ in ethanol under nitrogen for 4 h to give a yellow solution. An aqueous solution of KSCN was then added and the mixture allowed to stand for several days during which time the yellow *solid tri*-μ-*chloro-hexakis*(*ethyl diphenylphosphinite*)*diruthenium*(II) *thiocyanate* was deposited [ν(CN) 2 020 cm^{-1}] (Found: C, 58.2; H, 5.1; N, 0.8. Calc. for $C_{85}H_{90}Cl_3NO_6P_6Ru_2S$: C, 58.4; H, 5.1; N, 0.8%).

[{P(OEt)Ph$_2$}$_3$RuCl$_3$Ru{P(OEt)Ph$_2$}$_3$][SCN] (0.20 g) was then pyrolysed in n-propyl propionate (5 ml) at 120 °C to give the yellow *solid* (2).

In a similar fashion, pyrolysis of [{P(OEt)Ph$_2$}$_3$RuCl$_3$Ru{P(OEt)Ph$_2$}$_3$]X (X = [CN]$^-$ or [S$_2$PMe$_2$]$^-$) gave only (2).

def-*Tri*-μ-*bromo*-h-*diphenylphosphinito*-bgi-*tris*(*diphenylphosphinous acid*)-ac-*bis*(*ethyl diphenylphosphinite*)*diruthenium*(II) (3).—[{RuCl$_2$(C$_7$H$_8$)}$_n$] (0.22 g) was refluxed with excess of P(OEt)Ph$_2$ (0.50 ml) for 4 h in ethanol to give a yellow solution. This was reduced in volume and an excess of LiBr (0.25 g) added. The mixture was then pyrolysed at 120 °C for 12 h and the resulting yellow *crystals* filtered off and washed with ethanol and diethyl ether, m.p. 220 °C (Found: C, 52.9; H, 4.3; Br, 13.9; P, 11.4. Calc. for $C_{76}H_{73}Br_3O_6P_6Ru_2$: C, 53.4; H, 4.3; Br, 14.0; P, 10.9%).

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* Following the suggestion in ref. 14, we have used the term diphenylphospinite to describe P-bonded Ph$_2$PO$^-$ rather than the previously used diphenylphosphinate.

[18] '*X*-Ray' program system, Technical Report TR 192, Computer Science Center, University of Maryland, version of January 1974, implemented for the I.C.L. 4175 computer at the Edinburgh Regional Computing Centre.

[19] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.