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Transition-metal Complexes Containing Phosphorus Ligands. Part XI[1]. Cationic Trialkyl Phosphite Derivatives of Gold, Silver and the Platinum Metals

D. A. COUCH and S. D. ROBINSON
Department of Chemistry, King's College, Strand, London WC2R 2LS
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Ligand exchange reactions performed in polar solvents afford a convenient general route to an extensive series of cationic trimethyl and triethyl phosphite derivatives of gold, silver and the platinum metals, which were isolated as their tetraphenylborate salts. The products, which were characterised by elemental analysis, proton n.m.r. spectroscopy and conductivity measurements, contain cations of the general formulae $\{M[P(OR)_3]_6\}^{2+}$ *(M = Ru, Os);* $\{MX[P(OR)_3]_5\}^+$ *(M = Ru, X = H, Cl, Br, M = Os, X = Br);* $\{M[P(OR)_3]_5\}^+$ *(M = Rh, Ir);* $\{M[P(OR)_3]_4\}^{2+}$ *and* $\{MCl[P(OR)_3]_3\}^+$ *(M = Pd, Pt) and* $\{M[P(OR)_3]_4\}^+$ *(M = Ag, Au) (R = Me or Et throughout). A qualitative description of the coupling patterns observed in the proton n.m.r. spectra of these cations is given, and is interpreted in terms of ligand rearrangement, exchange and dissociation processes.*

Introduction

Studies of phosphorus donor ligands in transition-metal chemistry have traditionally centred on tertiary alkyl- and arylphosphines.[2] Only recently has emphasis been transferred in part to other potential phosphorus donors such as PH_3, PF_3 and trialkyl or triaryl phosphite esters $[P(OR)_3]$. Work on complexes containing trialkyl phosphites has been hampered by the very high solubility of their neutral transition-metal derivatives in organic solvents, and the strong tendency for the ligands to undergo scission at phosphorus–oxygen or oxygen–carbon bonds. Much of the early work in this field is typified by Russian studies,[3] on the trialkyl phosphite derivatives of the platinum metals, which gave products containing a variety of fragmented ligands including the species $P(O)(OR)_2^-$ and $PH(O)(OR)_2$, formed by hydrolysis and Michaelis–Arbuzov type rearrangement reactions. A few neutral transition-metal halide and hydride derivatives of the trialkyl phosphites have been isolated, and an extensive variety of substituted metal carbonyl complexes have also been reported.[4] However some of the most successful synthetic work to date in this field has relied upon the formation of ionic complexes to overcome solubility problems and facilitate isolation of products. Thus Troitskaya *et al.*[5] have reported synthesis of the cationic palladium(II) and platinum(II) derivatives $\{M[P(OR)_3]_4\}\{MCl_4\}$ and $\{M[P(OR)_3]_4\}Cl_2$ (R = alkyl). Other species more recently isolated as cations in complex salts include $\{Fe[P(OMe)_3]_6\}^{2+}$,[6] $\{Ru[P(OMe)_3]_6\}^{2+}$,[7] $\{Rh[P(OR)_3]_x\}^+$ (x = 4,5),[8] $\{RhH_2[P(OR)_3]_4\}^+$,[8] $\{RhHX[P(OR)_3]_4\}^+$,[8] $\{RhX_2[P(OR)_3]_4\}^+$,[8] $\{Co[P(OR)_3]_5\}^+$,[9,10] $\{Co[P(OR)_3]_6\}^{3+}$,[10] $\{Ni[P(OR)_3]_x\}^{2+}$ (x = 5,6),[10] $\{Cu[P(OR)_3]_4\}^+$,[11,12] $\{Ag[P(OR)_3]_4\}^+$,[10,12] and $\{NiH[P(OR)_3]_4\}^+$[13] (R = alkyl; X = halide), many of which were first reported while this present study[14] was in progress. Trialkyl phosphites are commonly regarded as weak σ-donor and strong π-acceptor ligands with relatively "soft" polarisable phosphorus donor atoms. These ligand characteristics find their counterpart in low oxidation state class "b" transition-metal ions, in particular those of gold, silver, (copper), and the six platinum metals. We have therefore undertaken a systematic study of cationic trialkyl phosphite complexes containing these ions, as part of our more extensive investigations on tertiary phosphite ligands, and have isolated a substantial range of these cationic species in the form of their tetraphenylborate salts.

Experimental

Phosphorus donor ligands were used as purchased. Triphenylphosphine and olefin complexes were prepared by standard literature procedures. ^1H n.m.r. spectra were recorded at 90, 100 and 220 MHz using Bruker HFX 90, Varian HA 100 and Varian HA 220 spectrometers respectively. Infrared spectra were obtained for nujol mulls using a Perkin–Elmer 457 grating spectrometer. Conductivities were measured for 10^{-3} molar solutions in acetonitrile using a Radiometer type CDM 2e conductivity meter. Analyses by Dr. Strauss, Oxford.

Synthesis of Complexes. General Technique

The techniques employed to synthesise, purify and characterise the complex salts are common for all members of the group. A general outline of the synthetic methods is therefore given. The reactions were performed by dissolving or suspending the appropriate transition-metal precursor in methyl cyanide or the appropriate alcohol, ROH, adding trialkyl phosphite, $P(OR)_3$, and then warming or boiling the mixture, if necessary, until a clear solution was obtained. Sodium tetraphenylborate, dissolved in the alcohol, ROH, was added to the clear solution, whereupon the required product precipitated immediately or crystallised slowly from the reaction solution. Precursors used were, $RuX_2(PPh_3)_3$, $[RuX_2(C_7H_8)]_n$, $RuHCl(PPh_3)_3$, $OsBr_2(PPh_3)_3$, $[IrHCl_2(C_8H_{12})]_2$, $PdCl_2(C_8H_{12})$, $PtCl_2(C_8H_{12})$, AgCl and $AuCl(C_8H_{14})$, all of which were prepared by standard literature procedures [hydrocarbon ligands are norbornadiene, C_7H_8; cyclo-octa-1,5-diene, C_8H_{12}; and cyclo-octene, C_8H_{14}].

The dicationic products generally precipitated from solution immediately on addition of the tetraphenylborate counter-ion and were purified by washing with chloroform or alcohol, in which they are only sparingly soluble, crystallising from dichloromethane/alcohol, and drying *in vacuo*. The monocationic products crystallised more slowly from the reaction solution, and were thus separated by fractional crystallisation. Traces of dications were eliminated by recrystallisation from chloroform/alcohol. The stoichiometry and ionic nature of the products were established by elemental analysis, conductivity measurements (MeCN solution) and proton n.m.r. spectroscopy. This latter technique gave the ratio of alkyl protons present and was particularly valuable in identifying complex ions.

Hexakis(trimethyl phosphite)ruthenium(II) tetraphenylborate and chloropentakis(trimethyl phosphite) ruthenium(II) tetraphenylborate

Trimethyl phosphite (4 ml) and *catena*-dichloro (bicyclo[2,2,1]hepta-2,5-diene)ruthenium (0.42 g) were heated under reflux in methanol (20 ml) until a clear yellow solution formed (*ca.* 1.5 h). Sodium tetraphenylborate (0.85 g) in methanol (10 ml) was added to the filtered reaction solution, and the white precipitate of hexakis(trimethyl phosphite)ruthenium(II) tetraphenylborate which immediately formed was filtered off, and washed successively with methanol and chloroform. Recrystallisation from dichloromethane–methanol gave the complex as white crystals (0.94 g, 40%).

The filtrate from the above synthesis, on standing for several days, deposited chloropentakis(trimethyl phosphite)ruthenium(II) tetraphenylborate. The complex was recrystallised from chloroform–methanol as white crystals (0.34 g, 20%).

Bromopentakis(trimethyl phosphite)ruthenium(II) tetraphenylborate

Trimethyl phosphite (2 ml) and *catena*-dibromo (bicyclo[2,2,1]hepta-2,5-diene)ruthenium (0.26 g) were heated under reflux in methanol (20 ml) until a clear yellow solution formed (*ca.* 30 min). Sodium tetraphenylborate (0.25 g) in methanol (10 ml) was added and the small yield of pale yellow precipitate which formed was filtered off. The filtrate, on standing, deposited white crystals of the required product. Recrystallisation from dichloromethane–methanol gave white rectangular plates (0.4 g, 47%).

Hydridotetrakis(trimethyl phosphite)(triphenylphosphine)ruthenium(II) tetraphenylborate and hydridopentakis(trimethyl phosphite)ruthenium(II) tetraphenylborate

Trimethyl phosphite (0.278 g) and chlorohydridotris (triphenylphosphine)ruthenium (0.415 g) were vigorously stirred together in methanol (20 ml) for 30 min. The clear orange–brown solution was treated with sodium tetraphenylborate (0.154 g) in methanol (10 ml) and the precipitate immediately formed was filtered off. The filtrate on standing deposited hydridotetrakis(trimethyl phosphite)(triphenylphosphine)ruthenium tetraphenylborate which was recrystallised from dichloromethane–methanol as white crystals [ν(RuH) = 1955 cm^{-1}] (0.26 g, 49%). The above product (0.63 g) and trimethyl phosphite (1 ml) were heated under reflux in benzene (5 ml) for 5 min, and the solution then evaporated under vacuum. The residual oil crystallised on addition of methanol and the solid was recrystallised from dichloromethane–methanol to yield hydridopentakis(trimethyl phosphite)ruthenium tetraphenylborate as white crystals [ν(RuH) = 1910 cm^{-1}] (0.27 g, 48%).

Chloropentakis(triethyl phosphite)ruthenium(II) tetraphenylborate

Triethyl phosphite (3 ml) and dichlorotris(triphenylphosphine)ruthenium (0.9 g) were heated under reflux in ethanol (20 ml) for 10 min. Sodium tetraphenylborate (0.34 g) in ethanol (5 ml) was added to the cooled clear yellow solution. After three days large colourless crystals of the required product were filtered off, washed with ethanol and dried *in vacuo*. The filtrate deposited a further crop of product (0.84 g, 70%).

Hydridopentakis(triethyl phosphite)ruthenium(II) tetraphenylborate

Triethyl phosphite (0.36 g) and chlorohydridotris (triphenylphosphine)ruthenium (0.4 g) in ethanol (20 ml) were shaken together for one hour. Sodium tetraphenylborate (0.15 g) in ethanol (5 ml) was added to the clear orange-brown reaction solution. After several days colourless crystals of the required product separated and were filtered off, washed with ethanol and dried *in vacuo* [ν(RuH) = 1910 cm^{-1}] (0.27 g, 50%).

Tri-μ-bromohexakis(triethyl phosphite)diruthenium tetraphenylborate

Triethyl phosphite (1.5 ml) was added to a suspension of *catena*-dibromo(bicyclo-[2,2,1]-hepta-2,5-diene) ruthenium (0.286 g) in ethanol (20 ml) and the mixture heated under reflux for 3 h. The filtered solution was treated with sodium tetraphenylborate (0.35 g) in ethanol (10 ml), set aside for one week, then evaporated under reduced pressure until the required product deposited as colourless crystals. These were filtered off, washed with a small volume of ethanol and recrystallised from dichloromethane–ethanol.

Bromopentakis(triethyl phosphite)osmium(II) tetraphenylborate

Triethyl phosphite (2.5 ml) and dibromotris(triphenylphosphine)osmium (0.36 g) were heated under reflux in ethanol (10 ml) for 30 min. The yellow solution was filtered and treated with sodium tetraphenylborate (0.13 g) in ethanol (5 ml); colourless crystals of the required complex deposited over a period of weeks and were recrystallised from chloroform–ethanol (0.40 g, 89%).

Hexakis(triethyl phosphite)osmium(II) tetraphenylborate

Triethyl phosphite (2.5 ml) and dibromotris(triphenylphosphine)osmium (0.44 g) were heated under reflux in acetonitrile (20 ml) for 30 min. Sodium tetraphenylborate (0.27 g) in ethanol (25 ml) was added to the clear orange solution. After 5 months the required product deposited as colourless crystals, these were washed with ethanol and chloroform then dried *in vacuo* (0.10 g, 14%). Reactions of trimethyl phosphite with dibromotris(triphenylphosphine)osmium in the presence of sodium tetraphenylborate give $[\mathrm{MePPh_3}]^+$ $[\mathrm{BPh_4}]^-$, identical with an authentic specimen prepared from triphenylphosphine, methyl iodide and sodium tetraphenylborate in methanol.

Tris(trimethyl phosphite)(cyclo-octa-1,5-diene) iridium(I) tetraphenylborate and pentakis(trimethyl phosphite)iridium(I) tetraphenylborate

Trimethyl phosphite (2 ml) and di-μ-chlorodichlorodihydridobis(cyclo-octa-1,5-diene)diiridium (0.90 g) were shaken together in methanol (30 ml) until only a trace of undissolved residue remained (*ca.* 10 min). Sodium tetraphenylborate (0.82 g) in methanol (20 ml) was then added to the filtered solution. A *colourless crystalline precipitate* of tris(trimethyl phosphite)(cyclo-octa-1,5-diene)iridium tetraphenylborate formed immediately, and was filtered off, washed with methanol and dried *in vacuo*.

The above product (1.09 g) and trimethyl phosphite (2 ml) were heated together under reflux in benzene (20 ml) for $1^1/_2$ h. The resultant solution was evaporated under reduced pressure to 10 ml then diluted with n-hexane (20 ml) to complete precipitation. The crystalline precipitate was filtered off, washed with n-hexane, dried *in vacuo* then recrystallised from dichloromethane–methanol to yield pentakis(trimethyl phosphite)iridium tetraphenylborate as large colourless air-sensitive prisms (0.56 g, 50%).

Pentakis(triethyl phosphite)iridium(I) tetraphenylborate

Prepared by an analogous method using ethanol in place of methanol (yield 50%).

Chlorotris(trimethyl phosphite)palladium(II) tetraphenylborate

Trimethyl phosphite (0.5 ml) and sodium tetraphenylborate (0.20 g) in methanol (10 ml) were added successively to a solution of dichlorobis(trimethyl phosphite)palladium (0.22 g) in methanol (10 ml). The resultant white precipitate was filtered off, washed with methanol, and recrystallised twice from dichloromethane–methanol to yield the required product as colourless crystals (0.065 g, 15%).

Chlorotris(triethyl phosphite)palladium(II) tetraphenylborate

Triethyl phosphite (0.23 g) in ethanol (10 ml) was added dropwise to a stirred solution of dichlorobis (triethyl phosphite)palladium (0.753 g) in ethanol (10 ml). Sodium tetraphenylborate (0.500 g) in ethanol (10 ml) was added to the reaction solution and the resultant white precipitate was filtered off, washed with ethanol, recrystallised four times from dichloromethane–ethanol by evaporation under reduced pressure, and dried *in vacuo* to yield the required product (0.57 g, 40%).

Pentakis(triethyl phosphite)palladium(II) tetraphenylborate

Triethyl phosphite (2.0 ml) and sodium tetraphenylborate (0.3 g) in acetonitrile (10 ml) were added successively to a solution of dichlorobis(triethyl phosphite)palladium (0.26 g) in acetonitrile (10 ml). The solution was diluted with ethanol, filtered and evaporated under reduced pressure until yellow needles formed, these were filtered off and washed with diethyl ether (0.40 g, 50%).

Tetrakis(triethyl phosphite)palladium(II) tetraphenylborate

Pentakis(triethyl phosphite)palladium tetraphenylborate was recrystallised three times from dichloromethane–ethanol, then washed with diethyl ether, and dried *in vacuo* to yield the required product as white crystals solvated with one mole of dichloromethane.

Yield 40%. This product reacted with triethyl phosphite in acetonitrile to regenerate pentakis(triethyl phosphite)palladium tetraphenylborate.

Chlorotris(triethyl phosphite)platinum(II) tetraphenylborate

Dichlorobis(triethyl phosphite)platinum (1.04 g) was dissolved in a solution of triethyl phosphite (0.29 g) in ethanol (20 ml). Sodium tetraphenylborate (0.59 g) dissolved in ethanol (5 ml) was added dropwise with vigorous stirring. The resultant white precipitate was filtered off, washed with ethanol, then twice recrystallised from dichloromethane–ethanol to yield the required product as colourless, irregular crystals (1.39 g, 76%).

Tetrakis(triethyl phosphite)platinum(II) tetraphenylborate

Triethyl phosphite (2 ml) and sodium tetraphenylborate (0.45 g) in ethanol (20 ml) were added successively to a solution of dichlorobis(triethyl phosphite) platinum (0.40 g) in ethanol (30 ml). The white precipitate was filtered off, and recrystallised from dichloromethane–ethanol to yield the required product as white crystals (0.50 g, 50%). (Proton n.m.r. confirms a triethyl phosphite : tetraphenylborate ratio of 2 : 1, and the presence of dichloromethane.)

Chlorotris(trimethyl phosphite)platinum(II) tetraphenylborate and tetrakis(trimethyl phosphite) platinum(II) tetraphenylborate

Attemps to prepare these compounds by reacting dichlorobis(trimethyl phosphite)platinum or dichloro (cyclo-octa-1,5-diene)platinum with trimethyl phosphite in methanol gave mixtures which could not be separated.

Tetrakis(trimethyl phosphite)silver(I) tetraphenylborate

Silver chloride (1.22 g) was dissolved in a solution of trimethyl phosphite (4 ml) in benzene (10 ml). Crystallisation of chloro(trimethyl phosphite)silver was initiated by evaporation under reduced pressure, and completed by addition of n-hexane. The above product (0.586 g) suspended in methanol (10 ml) dissolved rapidly on addition of trimethyl phosphite (0.5 ml). Sodium tetraphenylborate (0.75 g) in methanol (10 ml) was added to the clear solution where upon crystallisation of the product rapidly occurred. Recrystallisation from dichloromethane–methanol gave the required product as colourless crystals (1.4 g, 70%).

Tetrakis(trimethyl phosphite)gold(I) tetraphenylborate

Chloro(cyclo-octene)gold (0.95 g) dissolved in benzene (30 ml) was treated with trimethyl phosphite (0.4 ml) then filtered to remove precipitated gold. Crystallisation of chloro(trimethyl phosphite)gold was induced by evaporation under reduced pressure and completed by addition of n-hexane (20 ml); the complex was filtered off, washed with n-hexane and dried *in vacuo*.

The above product (0.29 g) was dissolved in methanol (20 ml) and treated successively with trimethyl phosphite (1.0 ml) and sodium tetraphenylborate (0.2 g) in methanol (10 ml). After three days colourless crystals of the required product were filtered off, washed with methanol and dried *in vacuo* (0.63 g, 75%).

Results and Discussion

Synthesis of Complexes

Ruthenium and osmium complex cations

The ruthenium(II) and osmium(II) cationic species $\{Ru[P(OR)_3]_6\}^{2+}$ and $\{Os[P(OEt_3]_6\}^{2+}$ afford the first examples of ruthenium and osmium ions coordinated to six equivalent, monodentate phosphorus donor ligands; the recently reported[5] iron(II) species, $\{Fe[P(OMe)_3]_6\}^{2+}$, completes this triad of cations. A series of monocations, $\{MX[P(OR)_3]_5\}^+$ (M = Ru, X = Cl, R = Me, Et; X = Br, R = Me; M = Os, X = Br, R = Et) were also isolated. These latter species are shown by n.m.r. spectroscopy *(vide infra)* to possess octahedral coordination with one unique axial and four equivalent equatorial phosphite ligands. The triad of cations, $\{MX[P(OR)_3]_3\}^+$ (M = Fe, Ru, Os; X = anionic ligand) is completed by the recently reported[5] synthesis of $\{Fe(SnCl_3)[P(OMe)_3]_5\}^+$. The system Ru/Br/P(OEt)$_3$ gave the binuclear cation $\{[(EtO)_3P]_3RuBr_3Ru[P(OEt)_3\}^+$ rather than the anticipated $\{RuBr[P(OEt)_3]_5\}^+$. Presumably the combination of bromide and triethyl phosphite ligands imposes stereochemical requirements which are best satisfied by the 3 : 3 coordination adopted in the dinuclear cation. Similar dinuclear species are obtained with the more bulky $P(OR)_2Ph$ and $P(OR)Ph_2$ ligands (R = Me, Et) and we attribute their formation to steric factors (unpublished results). The osmium based syntheses were hampered by lack of suitable labile osmium(II) olefin precursors. Syntheses from $OsBr_2(PPh_3)_3$ tended to be tediously slow, particularly for the cation $\{Os[P(OEt)_3]_6\}^{2+}$. Furthermore all attempts to prepare the osmium trimethyl phosphite derivatives $\{Os[P(OMe)_3]_6\}\{BPh_4\}_2$ and $\{OsBr[P(OMe)_3]_5\}\{BPh_4\}$ from $OsBr_2(PPh_3)_3$ were unsuccessful, the reactions giving instead substantial yields of $(MePPh_3)^+(BPh_4)^-$.

The ruthenium hydride, $RuHCl(PPh_3)_3$, reacted with excess trimethyl phosphite and sodium tetraphenylborate in *cold* methanol to yield the complex $\{RuH(PPh_3)[P(OMe)_3]_4\}\{BPh_4\}$, which, on further treatment with trimethyl phosphite in benzene, was converted to the pentakis(trimethyl phosphite) derivative $\{RuH[POMe)_3]_5\}\{BPh_4\}$. The corresponding triethyl phosphite

TABLE I.

Complex	Analytical C	Data[a] H	Conductivity ohm^{-1} mole^{-1} cm^2
$\{Ru[P(OMe)_3]_6\}\{BPh_4\}_2$	51.9(53.4)	6.25(6.4)	233
$\{RuCl[P(OMe)_3]_5\}\{BPh_4\}$	44.0(43.5)	6.35(6.1)	111
$\{RuBr[P(OMe)_3]_5\}\{BPh_4\}$	42.05(41.8)	6.1(5.85)	120
$\{RuH(PPh_3)[P(OMe)_3]_4\}\{BPh_4\}$	55.45(54.95)	6.25(6.15)	–
$\{RuH[P(OMe)_3]_5\}\{BPh_4\}$	45.35(44.95)	6.55(6.4)	–
$\{RuCl[P(OEt)_3]_5\}\{BPh_4\}$	50.7(50.4)	7.35(7.45)	95
$\{Ru_2Br_3[P(OEt)_3]_6\}\{BPh_4\}$	41.2(41.0)	6.05(6.3)	–
$\{RuH[P(OEt)_3]_5\}\{BPh_4\}$	51.95(51.8)	7.7(7.7)	93
$\{Os[P(OEt)_3]_6\}\{BPh_4\}_2$	56.05(55.25)	6.8(7.2)	–
$\{OsBr[P(OEt)_3]_5\}\{BPh_4\}$	46.25(45.65)	7.0(6.75)	96
$\{Ir[P(OMe)_3]_5\}\{BPh_4\}$	40.55(41.4)	5.6(5.8)	105
$\{Ir[P(OEt)_3]_5\}\{BPh_4\}$	48.1(48.3)	7.15(7.15)	109
$\{Pd[P(OEt)_3]_5\}\{BPh_4\}_2$	58.2(59.45)	7.3(7.35)	215
$\{Pd[P(OEt)_3]_4\}\{BPh_4\}_2 \times CH_2Cl_2$	58.35(58.65)	7.05(6.9)	–
$\{PdCl[P(OMe)_3]_3\}\{BPh_4\}$	47.4(47.55)	5.9(5.7)	127
$\{PdCl[P(OEt)_3]_3\}\{BPh_4\}$	52.5(52.55)	6.55(6.85)	98
$\{Pt[P(OEt)_3]_4\}\{BPh_4\}_2 \times {}^1/_2\, CH_2Cl_2$	56.7(56.3)	6.45(6.6)	227
$\{PtCl[P(OEt)_3]_3\}\{BPh_4\}$	48.3(48.1)	6.15(6.25)	88
$\{Ag[P(OMe)_3]_4\}\{BPh_4\}$			90
$\{Au[P(OMe)_3]_4\}\{BPh_4\}$			92

[a] Calculated figures given in parentheses.

complex $\{RuH[P(OEt)_3]_5\}\{BPh_4\}$ was obtained directly from $RuHCl(PPh_3)_3$ in cold ethanol. The presence of hydride ligands in the complexes $\{RuH[P(OR)_3]_5\}\{BPh_4\}$ and $\{RuH(PPh_3)[P(OMe)_3]_4\}\{BPh_4\}$ was confirmed by i.r. and high field n.m.r. spectroscopy (see experimental and Table II respectively). Other recently reported cationic hydrides of stoichiometry $[RuHL_5]^+$ (L = phosphorus donor ligand) include $\{RuH[PHPh_2]_5^{+}$[15] and $\{RuH[P(OMe)_2Ph]_5\}^+$;[7] the complex $\{RuH[P(OEt)_3]_5\}\{BPh_4\}$[7] has also been reported independently following the initial publication of our study.[14]

Rhodium and iridium complex cations

Our results on the rhodium–trialkyl phosphite system essentially confirm those previously reported by Haines;[8] accordingly we do not discuss them further. The iridium syntheses are based on the reaction of trialkyl phosphites with the iridium(III) complex, $[IrHCl_2(C_8H_{12})]_2$: in polar alcoholic solvents, ROH, the anionic ligands are displaced to yield the olefin complexes $\{Ir(C_8H_{12})[P(OR)_3]_3\}\{BPh_4\}$, which react further with excess trialkyl phosphite in a non-polar solvent (benzene) to afford the pentakis(trialkyl phosphite) derivatives $\{Ir[P(OR)_3]_5\}\{BPh_4\}$. These latter salts undergo slow decomposition in air; however, the products of decomposition do not appear to contain π-bonded tetraphenylborate ligands of the type found[16] in $Rh(BPh_4)[P(OR)_3]_2$. Synthesis of the iridium cations, $\{Ir[P(OR)_3]_5\}^+$ completes the triad $\{M[P(OR)_3]_5\}^+$ (M = Co, Rh, Ir). While this paper was in preparation Haines *et al.* reported synthesis and characterisation of the cationic species $\{Ir[P(OR)_3]_5\}^+$ and $\{Ir(C_8H_{12})[P(OR)_3]_3\}^+$; their results[17] essentially agree with our own.

Palladium and platinum complex cations

The palladium(II) and platinum(II) trialkyl phosphite systems give rise to two series of cations, $\{M[P(OR)_3]_4\}^{2+}$ and $\{MX[P(OR)_3]_3\}^+$. In addition, palladium affords the pentakis(triethyl phosphite) cation, $\{Pd[P(OEt_3]_5\}^{2+}$, thereby reflecting the increasing tendency to five coordination Pt^{II} < Pd^{II} < Ni^{II}. The unstable, air-sensitive palladium complexes, $\{Pd[P(OEt)_3]_4\}^{2+}$ and $\{Pd[P(OEt)_3]_5\}^{2+}$ may be interconverted by crystallisation in the absence or presence of excess free ligand. The related nickel derivatives $\{Ni[P(OR)_3]_x\}^{2+}$ (x = 5,6) have previously been reported.[10,12]

Silver and gold cationic complexes

These were isolated as light-sensitive crystalline solids $\{M[P(OR)_3]_4\}\{BPh_4\}$. The copper[11,12] and silver[10,12,18] cations $\{M[P(OR)_3]_4\}^+$ have previously been obtained as their nitrate or perchlorate salts; synthesis of the gold cation $\{Au[P(OMe)_3]_4\}^+$ therefore completes the triad. A very recent study[19] has afforded the bis(trimethyl phosphite) cation, $\{Au[P(OMe)_3]_2\}^+$, isolated as a nitrate or tetrafluoroborate salt. Conductivity measurements and n.m.r. spectra support our formulation of the silver and gold complexes as tetrakis derivatives $\{M[P(OR)_3]_4\}\{BPh_4\}$ (M = Ag, Au) but we were unable to obtain satisfactory analytical data for these rather unstable products.

TABLE II. N.m.r. spectroscopic data.

Complex Cation[a]	Ligand Site	$\tau(CH_3)$[d]	$\tau(CH_2)$[e]	$^3J(PH)Hz$	$^3J(HH')Hz$
$\{Ru[P(OMe)_3]_6\}^{2+}$[b]	–	6.28(v.c)	–	–	–
$\{RuCl[P(OMe)_3]_5\}^+$	eq.	6.37(v.c)	–	–	–
	ax.	6.56(d)	–	10.4	–
$\{RuBr[P(OMe)_3]_5\}^+$	eq.	6.36(v.c)	–	–	–
	ax.	6.53(d)	–	10.4	–
$\{RuCl[P(OEt)_3]_5\}^+$	eq.	8.74(t)	5.88(q)[f]	–	6.8
	ax.	8.78(t)	6.08(qn)	6.8	6.8
$\{Ru_2Br_3[P(OEt)_3]_6\}^+$	–	8.78(t)	5.91(m)	–	7.0
$\{RuH[P(OMe)_3]_5\}^+$	eq.	6.47(v.c)	–	–	–
	ax.	6.40(d)	–	7.0	–
	[RuH: τ19.6 complex pattern]				
$\{RuH(PPh_3)[P(OMe)_3]_4\}^+$	–	6.80(t)	–	$\lvert {}^3J(PH) + {}^5J(PH) \rvert = 10.4$	–
	–	6.60(d)	–	10.0	–
	–	6.45(d)	–	10.2	–
	[RuH: τ17.0–19.0 complex pattern]				
$\{RuH[P(OEt)_3]_5\}^+$	eq.	8.80(t)	6.09(q)[f]	–	7.0
	ax.	8.79(t)	6.07(q)[f]	–	7.0
	[RuH: τ19.8 complex pattern]				
$\{OsBr[P(OEt)_3]_5\}^+$	eq.	8.75(t)	5.90(q)[f]	7.0	7.0
	ax.	8.78(t)	6.05(qn)	7.0	7.0
$\{Rh[P(OMe)_3]_5\}^+$	–	6.45(s)	–	–	–
$\{Ir[P(OMe)_3]_5\}^+$	–	6.45(v.c)	–	–	–
$\{Ir[P(OEt)_3]_5\}^+$	–	8.80(t)	6.10(q)[f]	–	7.1
$\{Ir(C_8H_{12})[P(OMe)_3]_3\}^+$	–	6.45(v.c)[g]	–	$\lvert {}^3J(PH) + {}^5J(PH) \rvert = 11.25$	
$\{Ir(C_8H_{12})[P(OEt)_3]_3\}^+$	–	8.78(t)[g]	6.04(m)	–	7.1
$\{Pd[P(OEt)_3]_5\}^{2+}$[c]	–	8.75(t)	5.94(qn)	7.1	7.1
$\{Pd[P(OEt)_3]_4\}^{2+}$[c]	–	8.60(t)	5.66(q)	–	7.0
$\{PdCl[P(OMe)_3]_3\}^+$	–	6.38(s)	–	–	–
$\{PdCl[P(OEt)_3]_3\}^+$	–	8.73(t)	5.94(q)	–	7.0
$\{Pt[P(OEt)_3]_4\}^{2+}$[c]	–	8.64(t)	5.70(q)	–	7.1
$\{PtCl[P(OMe)_3]_3\}^+$[c]	–	6.16(s)	–	–	–
$\{PtCl[P(OEt)_3]_3\}^+$	–	8.72(t)	5.91(q)[f]	–	7.0
$\{Ag[P(OMe)_3]_4\}^+$	–	6.50(d)	–	11.5	–
$\{Au[P(OMe)_3]_4\}^+$	–	6.40(d)	–	11.0	–

[a] Spectra taken in $CDCl_3$ unless otherwise indicated. [b] CD_3CN Sol. [c] $(CD_3)_2CO$ Sol. [d] v.c. = virtual coupling, d = doublet, t = triplet, s = singlet slightly broadened by unresolved fine structure. [e] q = quartet, qn = quintet, m = multiplet. [f] Further fine structure evident but not fully resolved. [g] Olefin resonances *ca.* τ6.13 and τ7.4–7.6. [h] All spectra contained aryl proton resonances at *ca.* τ2.4–3.4; aryl/alkyl proton integrals were in accord with proposed stoichiometry for each complex.

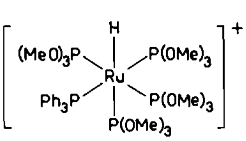
Confirmation of Structure and Stereochemistry. Analysis of Proton n.m.r. Data

The proton n.m.r. spectra of the coordinated trialkyl phosphite ligands present in the aforementioned complexes are complicated by virtual coupling interactions, ligand exchange processes, and stereochemical nonrigidity. A full analysis must therefore await the results of more detailed investigations including ^{31}P and variable temperature n.m.r. studies. In the present paper we offer a qualitative description of the spectra, salient features of which are given in Table II, and discuss the structural and stereochemical information which can be deduced from them by inspection.

Ruthenium and osmium complex cations

The methyl protons of the dication, $\{Ru[P(OMe)_3]_6\}^{2+}$ give rise to a symmetrical n.m.r. signal at τ 6.34 comprising a strong centre member flanked by two pairs of satellites, the outer pair of which are very sharp. This pattern, which appears to be characteristic of several rigid non-exchanging systems comprising six $P(OMe)_n R_{3-n}$ ligands (n = 1–3) in an octahedral configuration or four such ligands in a square planar configuration *(vide infra)*, has been previously reported for the rhodium[8] and iridium[17] complexes $\{M[P(OMe)_nPh_{3-n}]_4\}^+$ (n=1,2) and *trans*-$\{RhXY[P(OMe)_3]_4\}^+$ (X=Y=Br; X = H, Y = Br; X = Me, Y = I). For these latter complexes, containing four ^{31}P nuclei per molecule, a qualitative explanation has been given in terms of coupling between *cis* and *trans* pairs of ^{31}P nuclei giving rise to an $AA'A''A'''X_nX_n'X_n''X_n'''$ spin system.[8]

Cations of the type $\{MX[P(OMe)_3]_5\}^+$ (M = Ru; X = Cl, Br, H; M = Os, X = Br) give rise to a similar pattern of five lines (36 protons) attributable to the four equivalent $P(OMe)_3$ ligands in the equatorial plane, and an additional doublet pattern (9 protons) which is assigned to the unique axial $P(OMe)_3$ ligand. The doublet pattern, observed for the axial ligand, presumably arises from intraligand coupling $^3J(PH)$; there is no evidence of coupling with the ^{31}P nuclei of the equatorial $P(OMe)_3$ ligands. In the 100 MHz proton n.m.r. spectrum of the hydride complex, $\{RuH[P(OMe)_3]_5\}^+$, signals due to the axial and equatorial $P(OMe)_3$ groups overlap; however at 220 MHz this overlap is sufficiently resolved to allow the form of the spectrum to be unambiguously established. The intermediate product, $\{RuH(PPh_3)[P(OMe)_3]_4\}\{BPh_4\}$, obtained by reacting $RuHCl(PPh_3)_3$ with $P(OMe)_3$ and $NaBPh_4$ in cold methanol, contains aryl and alkyl protons in the required ratio 35:36. The pattern arising from the methoxy protons comprises doublets at τ 6.45 (9 protons) and τ 6.61 (9 protons), and a virtual coupling "triplet" at τ 6.82 (18 protons). This pattern strongly suggests the stereochemistry (1) for the complex cation,



(1)

with virtual coupling[20] involving the *trans* pair of equivalent $P(OMe)_3$ ligands.

The n.m.r. spectra of the triethyl phosphite dications, $\{M[P(OEt)_3]_6\}^{2+}$ show a well-resolved triplet pattern (54 protons) attributed to methyl protons in eighteen equivalent ethoxy groups. The resonance arising from the methylene protons comprises a 1:3:3:1 quartet (36 protons) broadened by partially resolved $^3J(PH)$ and $^5J(PH)$ couplings.

The proton n.m.r. spectra of the monocations, $\{RuCl[P(OEt)_3]_5\}^+$ and $\{OsBr[P(OEt)_3]_5\}^+$ are essentially similar. In each case the methyl protons generate a pair of sharp well-resolved but overlapping triplets (intensity ratio 1:4) consistent with the presence of one axial and four equivalent equatorial $P(OEt)_3$ ligands. In both complexes the methylene protons generate two overlapping signals (intensity ratio 1:4), which are separated at 220 MHz. The higher field signal, which we assign to the methylene protons of the unique, axial $P(OEt)_3$ ligand, comprises an apparent 1:4:6:4:1 quintet pattern, with the intraligand coupling constants $^3J(PH)$ and $^3J(HH)$ coincidently equivalent. The coincidental equivalence is reasonable since the corresponding couplings in the free ligand are 7.9 and 7.0 Hz respectively. The lower field signal (24 protons) assigned to the methylene protons of the four equivalent equatorial $P(OEt)_3$ ligands, comprises a quartet pattern [$^3J(HH)$] with broadening due to partially resolved phosphorus–hydrogen coupling. In the hydride complex cation, $\{RuH[P(OEt)_3]_5\}^+$, the chemical shift differences between equivalent protons on axial and equatorial $P(OEt)_3$ ligands are insufficient to permit complete resolution of separate signals even at 220 MHz; however the spectra appear to be of a form essentially similar to that observed for $\{RuCl[P(OEt)_3]_5\}^+$.

The high field n.m.r. spectra of the trimethyl and triethyl phosphite cations $\{RuH(PPh_3)[P(OMe)_3]_4\}^+$, $\{RuH[P(OMe)_3]_5\}^+$ and $\{RuH[P(OEt)_3]_5\}^+$ each contain, a complex, asymmetric irregular pattern centred at *ca.* τ 18.0–20.0. These spectra, which are entirely reproducible, are the subject of further investigations. Similar irregular high field n.m.r. patterns have been observed for the hydridic cation $\{IrH[P(OMe)_2Ph]_5\}^{2+}$;[21] however other complex cations of the type $[MH(L)_5]^{n+}$ including $\{RuH[P(OMe)_2Ph]_5\}^+$ give rise to simple, first order, high field patterns (doublet of quintets).[15,21]

The proton n.m.r. spectrum of the binuclear complex $\{[(EtO)_3P]_3RuBr_3Ru[P(OEt)_3]_3\}\{BPh_4\}$ shows the presence of aryl, methylene and methyl protons in the required ratio, 20:36:54. The signal due to the methylene protons is a symmetrical envelope with evidence of partially resolved fine structure; the methyl protons give rise to a sharp symmetrical triplet.

Rhodium and iridium complex cations

Haines reports[8] ligand equivalence on the n.m.r. time scale in the rhodium complex $\{Rh[P(OMe)_3]_5\}\{BPh_4\}$, and attributes this either to a rapid intramolecular trigonal-bipyramidal–tetragonal-pyramidal rearrangement equilibrium, or, alternatively, to a ligand dissociation process. Intraligand coupling between methyl and methylene protons in the triethyl phosphite derivative is observed; however the apparent absence of inter- or intraligand proton–phosphorus coupling in the trimethyl and triethyl phosphite derivatives suggests that ligand dissociation or fast exchange is occurring. Our n.m.r. results for these rhodium complexes essentially confirm those of Haines.[8]

In contrast we find that the proton n.m.r. spectra of the trimethyl phosphite iridium cations $\{Ir[P(OMe)_3]_5\}^+$ and $\{Ir(C_8H_{12})[P(OMe)_3]_3\}^+$ each contain a symmetrical virtual coupling pattern indicative of substantial inter- and intraligand proton–phosphorus coupling, and the absence of appreciable ligand dissociation. The apparent equivalence of the $P(OMe)_3$ ligands in each of these complexes points to the occurrence of a labile intramolecular rearrangement.

The proton n.m.r. spectra of the corresponding triethyl phosphite cations, $\{Ir[P(OEt)_3]_5\}^+$ and $\{Ir(C_8H_{12})[P(OEt)_3]_3\}^+$, also show evidence for the occurrence of a labile intramolecular rearrangement process. In each case the methyl protons give rise to a sharp, symmetrical triplet indicative of apparently equivalent triethyl phosphite ligands. The methylene protons of the cation $\{Ir[P(OEt)_3]_5\}^+$ give rise to a symmetrical quartet pattern, each member of which shows evidence for further unresolved fine structure; the corresponding resonance observed for $\{Ir(C_8H_{12})[P(OEt)_3]_3\}^+$ comprises a partially resolved symmetrical multiplet. The cyclo-octa-1,5-diene complexes, $\{Ir(C_8H_{12})[P(OR)_3]_3\}^+$, each show the proton n.m.r. pattern typical of the coordinated olefin. N.m.r. data recently reported by Haines *et al.*[17] for the cations $\{Ir[P(OR)_3]_5\}^+$ and $\{Ir(C_8H_{12})[P(OR)_3]_3\}^+$ (R = Me, Et) essentially confirm our results.

Palladium and platinum complex cations

These complexes are very labile, and in all cases ligand exchange processes occur sufficiently rapidly at room temperature to suppress all interligand coupling interactions. Thus the proton n.m.r. spectra of the complex cations $\{MCl[P(OEt)_3]_3\}^+$ and $\{M[P(OEt)_3]_4\}^{2+}$ (M = Pd, Pt) each comprise a quartet (methylene protons) and a triplet (methyl protons); slight broadening of the methylene quartet pattern provides the only evidence of proton–phosphorus coupling in these spectra. Likewise the proton n.m.r. spectra of the trimethyl phosphite cations, $\{MCl[P(OMe)_3]_3\}^+$ each comprise a slightly broadened singlet (methyl protons). In contrast the spectrum of the complex $\{Pd[P(OEt)_3]_5\}\{BPh_4\}_2$ contains a *quintet* [methylene protons, $^3J(PH) = {}^3J(HH)$] and a triplet [methyl protons]; similar patterns are also observed for the cations $\{M[P(OEt)_3]_4\}^{2+}$ in the presence of *ca.* 2 moles of added triethyl phosphite. On cooling these solutions the n.m.r. signal arising from the methylene protons reverts from a quintet to the more usual quartet pattern.

To account for the apparent absence of inter- and intraligand phosphorus–hydrogen coupling in the spectra of the complex cations $\{M[P(OEt)_3]_4\}^{2+}$ and $\{MCl[P(OR)_3]_3\}^+$, and the magnetic equivalence of the three trialkyl phosphite ligands present in the latter complexes we suggest that rapid ligand exchange processes are occurring. A similar explanation has recently been advanced[22] to account for the absence of interligand phosphorus–hydrogen coupling in the proton n.m.r. spectra of certain square-planar nickel(II) and platinum(II) methylphosphine derivatives at ambient temperature. The emergence of intraligand phosphorus–hydrogen coupling, $^3J(PH)$, in the spectra of the cations $\{M[P(OEt)_3]_4\}^{2+}$, on addition of excess free ligand, may be taken to indicate that the rate of ligand exchange is dependent upon free ligand concentration. Since the effect of cooling the sample is counter to the effect of adding free ligand we may reasonably conclude that the latter operation increases the rate of ligand exchange. This evidence is consistent with exchange occurring *via* formation of five coordinate intermediates similar to those proposed[23] for the phosphine, PR_3, catalysed *cis/trans* isomerisation of platinum(II) complexes, $PtX_2(PR_3)_2$.

Silver and gold complex cations

The proton n.m.r. spectra of the silver and gold complex cations $\{M[P(OMe)_3]_4\}^+$ comprise a doublet [$^3J(PH)$] which is fully resolved in the spectrum of the silver complex but only partially resolved for the gold derivative. By analogy with the palladium and platinum systems, the appearance of intraligand phosphorus–hydrogen coupling in the spectra of the silver and gold cations $\{M[P(OMe)_3]_4\}^+$ may be attributed to very rapid ligand exchange. This explanation is in accord with the rather labile nature of these complexes.

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