J. Chem. Soc. (A), 1966

Tris(triphenylarsine)- and Tris(triphenylstibine)-chlororhodium() Complexes and their Reactions with Hydrogen, Olefins, and Other Reagents

By J. T. Mague and G. Wilkinson

The complex compounds tris(triphenylarsine) - and tris(triphenylstibine) - chlororhodium(I) [RhCl(MPh₃)₃, M = As and Sb] have been prepared by interaction of MPh₃ with bis(ethylene)chlororhodium(I). The complexes generally show behaviour similar to that previously described for tris(triphenylphosphine)chlororhodium(I). Although the present complexes are not as efficient as the phosphine complex as homogeneous hydrogenation catalysts for olefins, they undergo similar chemical reactions with hydrogen, ethylene, diphenylacetylene, tetrafluoroethylene, hydrogen chloride, and oxygen. The complexes obtained in these reactions have been studied by infrared and nuclear magnetic resonance spectroscopy.

THE complex tris(triphenylphosphine)chlororhodium(I), RhCl(PPh₃)₃, is a most effective catalyst for the homogeneous hydrogenation of olefins and acetylenes in solution in organic solvents.¹ Also, the complex under-

goes a variety of novel addition and substitution reactions.2-5

We have now extended these studies by the prepar-

³ M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Comm.*, 1966, 129.
⁴ M. C. Baird and G. Wilkinson, *Chem. Comm.*, 1966, 267.
⁵ D. N. Lawson, J. A. Osborn, and G. Wilkinson, preceding

Paper.

J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.
 ² M. J. Mays and G. Wilkinson, J. Chem. Soc., 1965, 6629.

1737

ation of its triphenylarsine and triphenylstibine analogues, primarily to compare their relative efficiency as catalysts. The new complexes cannot be obtained in adequate yield directly from solutions of rhodium trichloride in ethanol in contrast to the phosphine case,¹ but they have been obtained indirectly by the action of an excess of the arsine or stibine on methanolic solutions of bis(ethylene)chlororhodium(I), $[(C_2H_4)_2RhCl]_2$.

The chemical behaviour of the trisarsine and trisstibine complexes generally resembles that of the phosphine complex.¹ In particular, as indicated by molecular-weight studies, both dissociate essentially completely in solutions in organic solvents such as benzene or chloroform so that solvent-occupied sites are available for addition reactions similar to those described for the phosphine.¹⁻⁵ The fact that many reactions occur so readily must be attributed to the co-ordinative unsaturation of the formally three-co-ordinate species, RhCl(MPh₃)₂, formed by this dissociation.

The triphenylstibine complex is the least stable of the three tris-complexes and some of its adducts, e.g., the cis-dihydrido-species, are unstable in the solid state. Further, other reactions, e.g., with carbon monoxide, give mixtures. Accordingly, the stibine complex is less amenable to study than either the phosphine or the arsine analogue.

Interaction with Molecular Hydrogen.—When solutions of RhCl(AsPh₃)₃ in chloroform, or other organic solvents, are treated with molecular hydrogen at $25^{\circ}/1$ atm., a hydrido-species, $RhCl(H_2)(AsPh_3)_2$, whose sixth position is assumed to be occupied by a solvent molecule, and which is evidently analogous to the phosphine species,¹ is obtained. The colour of the solutions in benzene and dichloromethane is yellow-orange, in chloroform greenish-yellow. The n.m.r. spectrum (Table) show two high-field lines of equal intensity, in contrast to the spectrum of the phosphine where the low-field line is split into a doublet by spin coupling of one proton with the ³¹P atom of the trans-triphenylphosphine group. This difference provides good confirmation of the octahedral nature of the hydrido-species,¹ in which there are two cis hydrogen atoms, one of which is trans to MPh₃, the other cis to two mutually cis MPh₃ groups and trans to halide. As for the phosphine complex, the n.m.r. lines are rather broad (half-width ca. 50 c./sec.) and show none of the fine structure expected, e.g., from coupling with ¹⁰³Rh. A similar explanation holds here too, namely the presence of traces of a paramagnetic species which can be detected by electron spin resonance. As before,¹ this contaminant is obtained in the preparation of the tris-species and cannot be separated from it; whether or not it can be formed by a slight disproportionation of the Rh^I complex to Rh⁰ and Rh^{II} is not yet clear.

By contrast with the *cis*-dihydrido-species $RhCl(H_2)(PPh_3)_2$ there is no appreciable dissociation of $RhCl(H_2)(AsPh_3)_2$ at 25° since the bound hydrogen cannot be displaced by sweeping with an inert gas. In addition, the hydrido-species in solution is not sensitive

The greater stability of the arsine hydrido-species is also shown by its inability to transfer hydrogen to an olefin such as hex-1-ene at 25° , as shown by the persistence of the high-field lines in the presence of injected olefin. The difference is accordingly reflected in the very considerably reduced catalytic ability towards homogeneous hydrogenation of olefins. With the techniques described earlier ¹ and under identical conditions with catalyst concentrations *ca.* 10^{-4} M in benzene and with cyclohexene as substrate, a negligible amount of hydrogen was absorbed at 25° during *ca.* 1 hr. At 40° , hydrogenation does occur at a measurable rate but this is only about 0.025 that observed for RhCl(PPh₃)₃ at 25° .

Since the *cis*-dihydrido-species in solutions in weakly co-ordinating solvents have a solvent-occupied site, comparatively rapid exchange between MPh₃ on the metal and MPh₃ in solution could be expected. The addition of a molar equivalent of PPh₃ to the chloroform solutions of RhCl(H₂)(AsPh₃)₂ causes immediate broadening of the two high-field lines and the appearance of a new weak and broad line approximately midway between them. At a Rh/PPh₃ ratio of 1:2, the characteristic three-line spectrum of RhCl(H₂)(PPh₃)₂ appears, with lines due to the mixed species still present but shifted to somewhat higher fields. At or above Rh/PPh₃ ratios of 1:3, the spectrum is essentially that of the phosphine complex only.

Similarly the addition of $AsPh_3$ at a $Rh/AsPh_3$ ratio of 1:3 to solutions of $RhCl(H_2)(PPh_3)_2$ produces lines due to the mixed species. However, even with very large excesses of the arsine it is not possible to eliminate the

Nuclear magnetic resonance and infrared spectra of hydrido-complexes

Complex	Solvent	τ	v _{м−н} (ст1)
RhClH ₂ (AsPh ₃) ₂	Benzene	$22 \cdot 1, 28 \cdot 3$	2022, 2042sh
	Chloroform	22.1, 29.0	2033, 2078sh
	Dichloromethane	22·1, 29·1	2030, 2051sh
RhClH ₂ (SbPh ₃) ₂	Chloroform	19.9, 27.9	2002, 2078
	Benzene	20.1, 30.1	
$RhCl_{2}H(AsPh_{3})_{2}$	Dichloromethane	25·9 ª	2069
RhCl ₂ H(SbPh ₃) ₂	Chloroform	28·3 ª	2014
^{<i>a</i>} $J_{\text{Rh}-\text{H}} = 6$ c./sec. (As), 7 c./sec. (Sb).			

phosphine splitting on the lines. Because there are a number of possible species present in the mixed phosphine-arsine solutions, it is not possible with the data available to treat the systems quantitatively. However it appears that the equilibrium lies appreciably on the side of the phosphine hydride species. In accord with this, the substitution of phosphine for arsine in the hydrido-species makes it possible to sweep out the bound hydrogen with an inert gas, as is the case for the pure phosphine species.¹

The stibine complex on hydrogenation also gives a *cis*dihydrido-species in solution (Table) which is similarly stable towards olefin at 25° and from which hydrogen cannot be removed by sweeping. Attempts to isolate a solid hydrido-species in this case failed and only illdefined materials which showed no Rh-H infrared stretching frequencies were obtained.

The catalytic activity of the stibine complex is even lower than that of the arsine; at 40° it appears to be about 0.05 times as effective in the hydrogenation of cyclohexene.

In connection with the postulate 1 of a solventoccupied site on the dihydrido-species it is noteworthy that when the triphenylarsine hydrido-species is crystallised from dichloromethane, the crystals analyse as $RhCl(H_2)(AsPh_3)_2, 0.5CH_2Cl_2$ (cf. the phosphine analogue ¹).

The solvent molecule is not readily removed by pumping at 25° although, when pumped for several days, samples showed signs of decomposition. We suggest that it is co-ordinated via the chlorine atoms so that CH₂Cl₂ is acting as a bridge between two hydridocomplex molecules. This rather strong co-ordination of dichloromethane is also observed for the hydrogen chloride and oxygen adducts, $RhCl_2H(AsPh_3)_2$ and $RhCl(O_2)(AsPh_3)_2$ (see below). We suggest that where formal oxidation to a rhodium(III) complex has occurred, octahedral co-ordination is preferred over pentacoordination and it appears that solvation by dichloromethane can be used as a diagnostic test for the formal oxidation state of the metal in these cases. By contrast the complexes $RhCl(L)(AsPh_3)_2$ where L is carbon monoxide, ethylene, tetrafluoroethylene, or diphenylacetylene, do not form solvates and are hence best formulated as square rhodium(I) complexes.

Interaction with Hydrogen Chloride.-The interaction of RhCl(PPh₃)₃ in chloroform or dichloromethane with hydrogen chloride leads to the adduct RhCl₂H(PPh₃)₂.³ Dichloromethane solutions of the arsine and stibine complexes react similarly, as shown by the appearance of a high-field doublet in the n.m.r. spectra of the solutions in each case (Table). The fact that coupling of the proton with ¹⁰³Rh is observed here, in contrast to the lack of resolution for the dihydrido-species, we attribute to the removal of the paramagnetic contaminant, presumably a rhodium(II) species, by oxidation with hydrogen chloride. The infrared spectrum of the adducts show only a single band in the Rh-H stretching region as is expected for a monohydrido-complex.

It was impossible to obtain reliable analytical results on the isolated solids, although good crystalline products were initially obtained, owing to the rapid loss of hydrogen chloride and also of dichloromethane at room temperature. This decomposition is accompanied by the destruction and darkening of the crystals. The results do indicate, however, that there are only two molecules of arsine or stibine and at least two chlorine atoms present per metal atom. A weight-loss determination on the solid showed that during a few hours, at

J. Chem. Soc. (A), 1966

room temperature, 85-90% decomposition occurred, corresponding approximately to the loss of one molecule of hydrogen chloride and half a molecule of dichloromethane per rhodium atom. It seems reasonable to conclude that the crystals are of a binuclear species with a bridging co-ordinated dichloromethane, namely [RhCl₂H(MPh₃)₂]₂,CH₂Cl₂. Interaction of the arsine complex in chloroform solution with carbon monoxide rapidly produces the known complex RhCl(CO)(AsPh₃)₂.6

Interaction with Olefins.—As with the phosphine,¹ a crystalline ethylene complex, $RhCl(C_2H_4)(AsPh_3)_2$ can be isolated by interaction of RhCl(AsPh₃)₃ with ethylene in an organic solvent; the same complex can be obtained by treating a benzene solution $[(C_2H_4)_2RhCl]_2$ with two equivalents of arsine at 25°. The n.m.r. spectrum of chloroform solutions of the complex has a single sharp line at $\tau = 7.26$ which is unchanged in position and appearance on cooling to -60° . In presence of excess of ethylene, the line position moves downfield, approaching that of free ethylene ($\tau = 4.68$) as the ethylene concentration increases. However, the higher τ values found for the arsine complex indicate that the exchange rate of bound and free ethylene is slower than in the phosphine case, *i.e.*, the ethylene is less labile here. This is also shown by the fact that passage of an inert gas through a solution of the complex does not readily displace ethylene. The infrared spectrum of the complex shows a band at 1210 cm.⁻¹ and two bands at ca. 950 cm.⁻¹ which are similar in position and appearance to those in the ethylene complex $[(C_2H_4)_2RhCl]_2$.⁷ However, there is no band in the 2000-1500 cm.⁻¹ region where absorption due to co-ordinated C=C is expected. The ethylene in the complex is readily displaced by carbon monoxide to give RhCl(CO)(AsPh₃)₂.

The complex with tetrafluoroethylene,

 $RhCl(C_2F_4)(AsPh_3)_2$, is similar to the phosphine analogue.² Its ¹⁹F n.m.r. spectrum has a sharp doublet $(J_{\rm Rh-F} = 8 \text{ c./sec.})$ centred at 33.5 p.p.m. on the highfield side of benzotrifluoride (internal standard). As for the phosphine complex, this resonance is insensitive to the presence of excess of $\mathrm{C}_2\mathrm{F}_4$ indicating absence of exchange of bound and free ligand.

The arsine and stibine complexes in solution react rapidly with butadiene, the colour of the solutions changing from red-brown to yellow or orange accompanied by vigorous effervescence and the evolution of heat. However, solid complexes could not be isolated.

Interaction with Diphenylacetylene.-Both the phosphine and arsine complexes react with diphenylacetylene to give stable species, $RhCl(Ph_2C_2)(MPh_3)_2$ (M = P or As). These have a strong infrared band at ca. 1900 cm.-1 which is only slightly below the stretching region of co-ordinated C≡C groups in other acetylene complexes⁸ and suggests that the acetylene is acting as a simple donor ligand in a square rhodium(1) complex. Molecularweight measurements indicate that the phosphine

⁶ L. Vallarino, J. Chem. Soc., 1957, 2287.
⁷ R. D. Cramer, Inorg. Chem., 1962, 1, 722.

⁸ J. L. Boston, S. O. Grim, and G. Wilkinson, J. Chem. Soc., 1963, 3468.

complex dissociates in solution while the arsine complex does not. Both complexes in solution react readily with carbon monoxide however to produce the carbonyl complexes $RhCl(CO)(MPh_{a})_{a}$ (M = P or As).

Tris(triphenylstibine)chlororhodium(I) also reacts with diphenylacetylene in dichloromethane. A red solid is obtained but the analytical results could not be fitted to a unique formula and attempts to recrystallise the material, even in the presence of excess of diphenylacetylene, led only to decomposition. In this respect it resembles the phosphine complex which also cannot be recrystallised. The solid shows two infrared bands at 1893 and 1902 cm.⁻¹.

Reactions with Carbon Monoxide and Aldehydes.—The arsine complex in benzene or chloroform reacts rapidly at 25° with carbon monoxide to produce the complex RhCl(CO)(AsPh₃)₂⁶ and the same complex is obtained by abstraction of carbon monoxide from aldehydes. In refluxing benzene the latter reaction is rapid, but several days are required at 25°. Both reactions are similar to those of the phosphine complex.^{1,3}

With carbon monoxide the stibine complex gives a mixture which we have been unable to separate. From the reaction with heptaldehyde in refluxing benzene, red crystals were obtained which have a single CO stretch at 1962 cm.⁻¹. Although our analytical results are not too satisfactory the compound appears to be similar to the stibine complex reported by Vallarino.⁶

Reaction with Oxygen.—In dichloromethane the arsine complex readily absorbs one mol. of oxygen and the isolated adduct shows a rather broad infrared band at 892 cm.⁻¹ with a shoulder at 886 cm.⁻¹ (Nujol mull). This lies in the range where bands due to co-ordinated oxygen have been recorded.⁹ Analyses of the product so prepared were not very satisfactory but it is clear that one molecule of oxygen and two molecules of arsine are present per metal atom. The oxygen-containing adduct reacts readily with carbon monoxide in chloroform to produce RhCl(CO)(AsPh₃)₂ indicating that the oxygen is most likely co-ordinated directly to the metal atom and that no triphenylarsine oxide is present. The chlorine content of the samples were consistently high when prepared in dichloromethane, indicating that they contained some solvent which is presumably coordinated.

An unsolvated sample of the oxygen adduct having the formula $RhCl(O_2)(AsPh_3)_2$ was isolated when the preparation of $RhCl(AsPh_3)_3$ was attempted in air. The similarity of its infrared spectrum to that of samples prepared from $RhCl(AsPh_3)_3$ and oxygen in dichloromethane suggests that the latter should be formulated $RhCl(O_2)AsPh_3)_2,nCH_2Cl_2$.

EXPERIMENTAL

Microanalyses and molecular weights (Mechrolab osmometer, 37°) were by the Microanalytical Laboratory, Imperial College, and by Dr. A. Bernhardt, Mülheim. Infrared spectra (Nujol mulls unless otherwise specified) were recorded on a Grubb-Parsons "Spectromaster" grating instrument; all compounds had bands due to AsPh₃ or SbPh₃ and only additional peaks are listed. N.m.r. spectra were obtained on a Varian V-4311 spectrometer at 56.45 Mc./sec. Melting points were determined on a conventional hot-stage microscope and are uncorrected.

Reagent grade chemicals were used. All solvents were degassed before use and most reactions were carried out in nitrogen; other techniques and materials have been described.¹ All compounds are moderately soluble in benzene and chlorinated hydrocarbons.

Bis(ethylene)chlororhodium(1).—This was prepared by a modification of Cramer's procedure.⁷ Rhodium trichloride thriydrate (1 g.) was dissolved in 5 ml. of degassed, 10% aqueous methanol in a thick-walled glass tube. Ethylene (Matheson CP grade, *ca.* 3 ml.) was condensed in and the sealed tube shaken vigorously for 2 hr. The orange crystals (0.48 g., yield 65% based on Rh) were collected, dried in a nitrogen stream, and used immediately. The filtrate could be treated again with ethylene to produce an additional small amount of complex. The infrared spectrum and m. p. of the product were essentially identical with those reported by Cramer.⁷

Triphenylarsine Complexes.—Tris(triphenylarsine)chlororhodium(1). To a solution of triphenylarsine (5 g., Eastman White Label) in hot methanol (15 ml.) under nitrogen was added bis(ethylene)chlororhodium(I) (0.2 g.) and the solution refluxed for 20 min. Nitrogen-saturated anhydrous diethyl ether (15 ml.) was then added and the solution refluxed until brown crystals of the complex, m. p. 150-155° (decomp.), were deposited. These were collected, washed with diethyl ether, and dried in vacuo {yield 0.61 g., 56% based on $[(C_2H_4)_2RhCl]_2$ [Found: C, 60.8; H, 4.2; Cl, 3.5%; *M*, 506 (CHCl₃), 683 (C₆H₆). C₅₄H₄₅As₃ClRh requires C, 61·4; H, 4·3; Cl, 3·4%; M, 1057]. Even when good precautions to exclude air are taken, the product is often contaminated with a small amount of an oxygencontaining material. This contamination could be minimised by thorough degassing of the solvents and by ensuring that the ether is peroxide-free.

Bis(triphenylarsine)-cis-dihydridochlororhodium(III) dichloromethane solvate. The arsine complex above (0·2 g.) was dissolved in hydrogen-saturated dichloromethane (5 ml.) and the solution concentrated in a hydrogen atmosphere. On addition of diethyl ether, the yellow complex precipitated; it was collected, washed with diethyl ether, and dried in vacuo (yield 0·11 g., 75% based on Rh) (Found: C, 55·8; H, 4·3; Cl, 8·9. C_{38·5}H₃₃As₂Cl₂Rh requires C, 55·2; H, 4·2; Cl, 8·9%). The compound is fairly stable in solution and in the solid state in air but tends to darken upon prolonged (several days) exposure; ν_{max} . 2051sh (Rh-H str., CH₂Cl₂ solution), 2030m (Rh-H str., CH₂Cl₂ solution), 1275m, 1119w, 804m (Rh-H bend) cm.⁻¹.

Bis(triphenylarsine)ethylenechlororhodium(I). To ethylene-saturated dichloromethane (5 ml.) was added RhCl(AsPh₃)₃ (0·2 g.). An atmosphere of ethylene was maintained over the clear yellow solution while diethyl ether (5 ml.) was added. The yellow microcrystals of the *complex*, m. p. 163° (decomp.), which soon formed were collected, washed with diethyl ether, and dried *in vacuo* (yield 0·12 g., 80%) (Found: C, 58·1; H, 4·5; Cl, 5·1. C₃₈H₃₄As₂ClRh requires C, 58·5; H, 4·4; Cl, 4·5%); ν_{max} , 1304m, 962m, 949m cm.⁻¹.

⁹ L. Vaska, Science, 1963, 140, 809.

Bis(triphenylphosphine)diphenylacetylenechlorohodium (1). Tris(triphenylphosphine)chlororhodium (1) (0.46 g.) was dissolved in hot benzene (20 ml.) and added to a solution of diphenylacetylene (0.1 g.) in hot benzene (5 ml.). The solution was boiled for 2 min. and set aside to cool whereupon yellow crystals of the complex, m. p. 157–163° (decomp.), slowly separated from the orange solution (yield 0.25 g., 60%) [Found: C, 71.5; H, 4.9; Cl, 4.5%; M, 408 (CHCl₃). C₅₀H₄₀ClP₂Rh requires C, 71.4; H, 4.8; Cl, 4.7%; M, 840]; v_{max} , 1916s (C=C str.) cm.⁻¹.

The complex is soluble in benzene, chloroform, methlyene chloride, and acetone. It dissociates in solution and cannot be recrystallised. It is a non-conductor in nitrobenzene solution.

Bis(triphenylarsine)diphenylacetylenechlororhodium(1).

Dichloromethane (ca. 5 ml.) solutions of diphenylacetylene (0·1 g.) and RhCl(AsPh₃)₃ (0·2 g.) were mixed under nitrogen. The dark brown solution rapidly lightened in colour and orange crystals of the *complex*, m. p. 218—220° (decomp.), formed. They were collected, washed with diethyl ether, and dried *in vacuo* (yield 0·16 g., 90%) [Found: C, 64·6; H, 4·5; Cl, 3·9%; *M*, 906 (CHCl₃). C₅₀H₄₀As₂ClRh requires C, 64·7; H, 4·3; Cl, 3·8%; *M*, 929]; ν_{max} . 1883s (C=C str., CHCl₃ sol.) cm.⁻¹.

Bis(triphenylarsine)tetraftuoroethylenechlororhodium(1). A dichloromethane (5 ml.) solution of RhCl(AsPh₃)₃ (0·2 g.) was treated with excess of tetrafluoroethylene in a sealed glass tube at 25°. When the solution was light orange the tube was opened and light petroleum (b. p. 60–80°) was added until the solution become cloudy. After standing for 22 hr. at -5° , the yellow-orange precipitate of the complex, m. p. 86–88°, was collected, washed with diethyl ether, and dried in vacuo (yield 0·13 g., 80%) [Found: C, 53·9; H, 4·0; F, 8·7%; M, 875 (cryoscopic in C₆H₆). C₃₈H₃₀As₂ClF₄Rh requires C, 53·6; H, 3·6; F, 8·9%; M,

J. Chem. Soc. (A), 1966

851]; ν_{max} 1263m, 1113vs, 1033vs, 813vs, 798s, 788s, 679s cm. $^{-1}$

Interaction of RhCl(AsPh₃)₃ with HCl. Hydrogen chloride was passed into a solution of RhCl(AsPh₃)₃ in dichloromethane at 0°. The dark brown colour rapidly lightened to orange and addition of diethyl ether precipitated a yellow microcrystalline solid. An analogous treatment of RhCl(SbPh₃)₃ gave a red-brown material.

Interaction of RhCl(AsPh₃)₃ with oxygen. On passing oxygen into solutions of the complex in dichloromethane these became greenish-brown. Olive solids were obtained upon addition of diethyl ether. On one occasion when the preparation of RhCl(AsPh₃)₃ was attempted with no precaution taken to exclude air (methanol solution), brown crystals were obtained which exhibited an infrared band at *ca.* 890 cm.⁻¹. The analysis corresponded to the unsolvated complex RhCl(O₂)(AsPh₃)₂ [Found: C, 55·5; H, 4·3; O, 4·0%; M, 740 (CHCl₃). C₃₈H₃₀As₂ClO₂Rh requires C, 55·3; H, 3·9; O, 4·1%; M, 783].

Triphenylstibine Complexes.—These were prepared by entirely analogous methods with similar quantities.

Tris(triphenylstibine)chlororhodium(I). A bright purple powder decomposing without melting at 170° was obtained {yield ca. 50% based on $[(C_2H_4)_2RhCl]_2$ } [Found: C, 54·0; H, 3·7; Cl, 2·8%; M, 608 (CHCl₃). C₅₄H₄₅Sb₃ClRh requires C, 54·2; H, 3·8; Cl, 2·9%; M, 1197].

We are indebted to the National Institute of Health, Bethesda, Maryland, for a Post-doctoral Fellowship (J. T. M.). Thanks are also due to Johnson Matthey Ltd. for generous loans of rhodium trichloride, and to Dr. J. A. Osborn for assistance with catalytic experiments.

INORGANIC RESEARCH LABORATORIES,

 IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,

 LONDON S.W.7.
 [6/593 Received, May 18th, 1966]