Transition-metal Complexes containing Phosphorus Ligands. Part III.[1] Convenient Syntheses of Some Triphenylphosphine Complexes of the Platinum Metals

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Convenient, single-stage syntheses have been devised for a range of important hydride-, carbonyl-, and nitrosyl-containing triphenylphosphine complexes of the platinum metals. The reactions are performed in homogeneous, alcoholic solutions from which the required products precipitate or crystallise cleanly; sodium borohydride, aqueous formaldehyde, and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide are used as convenient sources of hydride, carbonyl, and nitrosyl ligands respectively. Abstraction of hydrogen chloride to form co-ordinatively unsaturated derivatives is achieved by introduction of triethylamine to the reaction solution. New compounds prepared and characterised include $[OsH_4(PPh_3)_3]$ and $[Ru(NO)_2(PPh_3)_2]$. The latter compound is the first well characterised dinitrosyl of ruthenium.

THE growing importance of triphenylphosphine complexes of the platinum metals and their widespread use as catalysts and as precursors for other derivatives prompted this study of convenient preparative routes to some of these compounds.[2] Literature methods for the preparation of hydride-, carbonyl-, and nitrosyl-containing triphenylphosphine derivatives of the platinum metals frequently involve multistage reactions or reactions under heterogeneous conditions. Hydrogen, carbon monoxide, nitric oxide, and nitrosyl halides are commonly used to provide hydride, carbonyl, and

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[2] A preliminary report of part of this work has previously been published: J. J. Levison and S. D. Robinson, *Chem. and Ind.*, 1969, 1514.

nitrosyl ligands in these preparations.[3,4] The syntheses described here are performed in single stages under essentially homogeneous conditions and employ sodium borohydride, aqueous formaldehyde, and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in place of the more hazardous gases as sources of the required ligands. Sodium borohydride is also used throughout as reducing agent, being more convenient than the aluminium hydride and alkyl complexes.

The reaction conditions employed permit the achievement of a high degree of selectivity and control in these syntheses. Thus, changes in reaction temperature and solvent, concentration of ligand, or nature of reagents provide routes to a range of pure complexes. Furthermore, the low solubility of most triphenylphosphine complexes in the alcoholic solvents used in these reactions ensures the rapid precipitation or crystallisation of the required product in good yield. A summary of reagents, solvents, and products for the major reactions discussed is given in the Table.

Reagents	$RhCl_3$ aq.	$RuCl_3$ aq.	Na_2IrCl_6 aq.	Na_2OsCl_6 aq.
$PPh_3 + NaBH_4$ [a]	$[RhH(PPh_3)_4]$ [c]	$[RuH_2(PPh_3)_4]$ [c]		
$PPh_3 + NaBH_4$ [b]			*mer*-$[IrH_3(PPh_3)_3]$	$[OsH_4(PPh_3)_3]$
$PPh_3 + NaBH_4 +$ aq. HCHO [a]	$[RhH(CO)(PPh_3)_3]$	$[RuH_2(CO)(PPh_3)_3]$		
$PPh_3 + NaBH_4 +$ aq. HCHO [b]		$[Ru(CO)_3(PPh_3)_2]$	$[IrH(CO)(PPh_3)_3]$	
$PPh_3 +$ aq. HCHO [b]		$[RuHCl(CO)(PPh_3)_3]$	$[IrHCl_2(CO)(PPh_3)_2]$	
$PPh_3 +$ aq. HCHO [b]			$[IrHCl_2(PPh_3)_3]$ [c]	
$PPh_3 +$ aq. HCHO $+ NEt_3$ [b]			$[IrCl(CO)(PPh_3)_2]$	
$PPh_3 +$ MNTS [a,d]	$[RhCl_2(NO)(PPh_3)_2]$	$[RuCl_3(NO)(PPh_3)_2]$		
$PPh_3 +$ MNTS [b]			$[IrCl_2(NO)(PPh_3)_2]$	$[OsCl_3(NO)(PPh_3)_2]$
$PPh_3 + NaBH_4$ [a] + MNTS [a]	$[Rh(NO)(PPh_3)_3]$	$[Ru(NO)_2(PPh_3)_2]$		

[a] Boiling ethanol solution. [b] Boiling 2-methoxyethanol solution. [c] Large excess of PPh_3 required. [d] MNTS = *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide.

The basic technique applied to each preparation involves the addition of a solution of the appropriate metal salt to a well stirred, boiling, alcoholic solution of triphenylphosphine; solutions of sodium borohydride, aqueous formaldehyde, or *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide are rapidly added as required and the mixture is heated until precipitation occurs, or until reaction is complete (usually *ca.* 2—15 min). The reaction mixtures are then cooled and filtered and the products purified as necessary. The efficiency and selectivity of most of the syntheses described is testified by the high yields obtained and, in many cases, by the good analytical and spectroscopic data recorded for unrecrystallised products. Precipitation of unwanted intermediates, leading to contamination of the final product is a possible hazard of these reactions but in our experience it did not arise provided that the reaction conditions were rigorously controlled. In particular, rapid successive addition of the various reagents is essential once the reaction has been commenced. In appropriate cases, the total reduction of the metal halide was confirmed by blank halide analyses obtained on the products in addition to the usual analytical and spectroscopic data. The average time for a complete preparation (*ca.* 30 min) and the simplicity of the technique offer considerable advantages over literature syntheses.

In most of the syntheses described, platinum metals were introduced in the form of chlorides or chloro-anions, since use of the corresponding bromo-species frequently altered the course of the reactions. This behaviour is discussed with particular reference to a series of reactions involving sodium chloroiridate and sodium bromoiridate. Small changes in the structure of the phosphine ligands also change the course or lower the efficiency of many of the reactions. Thus, attempts to perform analogous preparations with tri-*p*-tolyl, tri-*p*-anisyl, and tri-*p*-chlorophenylphosphines frequently failed or gave very poor yields. Further studies involving these and other phosphines are in progress and will be reported elsewhere.

Hydride Complexes.—Reductions of aqueous ethanolic solutions of sodium chloropalladite or sodium chloroplatinite by sodium borohydride in the presence of excess of triphenylphosphine have been used to synthesise tetrakis(triphenylphosphine)-palladium and -platinum respectively.[5] A related sodium borohydride reduction of $[K_2ReI_6]$ in the presence of excess of triphenylphosphine was used [6] to synthesise $[ReH_5(PPh_3)_3]$.

Our studies now reveal that similar reactions involving rhodium, ruthenium, iridium, and osmium chlorides or chloro-anions may be used to prepare $[RhH(PPh_3)_4]$, $[RuH_2(PPh_3)_4]$, *mer*-$[IrH_3(PPh_3)_3]$, and $[OsH_4(PPh_3)_3]$ respectively. A convenient synthesis of $[\alpha\text{-}IrCl_2H(PPh_3)_3]$ has also been devised and is described in the next section.

Previous syntheses of $[RhH(PPh_3)_4]$ have utilised aluminium alkyls,[7] Grignard reagents,[8] or hydrogen at high pressure [9] as reductants. Reduction of $[RhCl(PPh_3)_3]$ by hydrazine [10] or sodium propoxide [11] in the presence of triphenylphosphine has also been employed. Addition of triphenylphosphine to $[RhH(PPh_3)_3]$ to

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form $[RhH(PPh_3)_4]$ has recently been reported.[10,12] The closely related ruthenium complex $[RuH_2(PPh_3)_4]$ has previously been prepared by reduction of ruthenium species by $AlEt_2(OEt)$ in the presence of excess of triphenylphosphine.[7,13] In the present method, ethanolic solutions of rhodium trichloride and sodium borohydride are added in rapid succession to a vigorously stirred solution of triphenylphosphine in boiling ethanol. If large molar ratios of triphenylphosphine to rhodium salt are used (10 : 1) orange, crystalline $[RhH(PPh_3)_4]$ separates in excellent yield; with smaller ratios (5 : 1), an orange-red solid, apparently $[RhH(PPh_3)_3]$,[10,12] is deposited. The exact nature of this latter product is unconfirmed and its preparation somewhat irreproducible; we do not therefore discuss it further. Similar reactions involving hydrated ruthenium trichloride in place of rhodium trichloride give $[RuH_2(PPh_3)_4]$ as mustard yellow microcrystals, or $[RuH_2(PPh_3)_3]$ as a light brown powder, depending on the molar excess of phosphine present in the solution. The identity of the latter complex was supported by analytical and spectroscopic data, and by reactions with formaldehyde, triphenylphosphine, and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide to yield $[RuH_2(CO)(PPh_3)_3]$ (white isomer), $[RuH_2(PPh_3)_4]$, and $[Ru(NO)_2(PPh_3)_2]$ respectively. During the preparation of the ruthenium triphenylphosphine dihydride complexes, intermediate formation of $RuClH(PPh_3)_3$ is indicated by a transient and characteristic deep purple colour when approximately 50% of the sodium borohydride solution has been added; crude $[RuClH(PPh_3)_3]$ (ν_{RuH} 2020 cm^{-1}) [14] can be isolated from these purple solutions by evaporation of the solvent under reduced pressure. It is interesting to note that reduction of $[RuCl_2(PPh_3)_3]$ by aqueous sodium borohydride in a nonpolar solvent, benzene, proceeds only to the monohydride stage and is a standard preparation of the complex $[RuClH(PPh_3)_3]$.[14] We have shown previously [2] that *X*-ray powder photographs of the complexes $[Pd(PPh_3)_4]$, $[RhH(PPh_3)_4]$, and $[RuH_2(PPh_3)_4]$, prepared by the sodium borohydride reduction technique, are identical and we have tentatively suggested, on the basis of this evidence, that the molecules may have closely similar structures (comprising a tetrahedral arrangement of phosphine ligands about the metal atom with the hydride ligands situated on C_3 axes). This suggestion has been fully confirmed in the case of $[RhH(PPh_3)_4]$ by a recently reported,[15] full crystal structure determination, which shows that within experimental limits the RhP_4 skeleton is tetrahedral.

Salts of iridium and osmium are reduced by sodium borohydride in the presence of excess of triphenylphosphine to give modest yields of *mer*- and *fac*-$[IrH_3(PPh_3)_3]$ and $[OsH_4(PPh_3)_3]$, respectively. By suitable adjustment of technique, pure *mer*-$[IrH_3(PPh_3)_3]$ may be isolated. $[IrH_3(PPh_3)_3]$ (*mer*- and *fac*-isomers) have previously been synthesised by reduction of iridium tribromide with ethanolic sodium borohydride in the presence of triphenylphosphine.[16] Reduction of $[IrCl_2H(PPh_3)_3]$ with lithium aluminium hydride in tetrahydrofuran has also been employed to prepare pure *mer*-$[IrH_3(PPh_3)_3]$.[17] $[OsH_4(PPh_3)_3]$ had not been prepared previous to this work and was one of the first osmium tetrahydrides to be reported.[18,19] We now find that addition of ethanolic solutions of sodium chloroiridate and sodium borohydride to a boiling, ethanolic solution of triphenylphosphine gives rapid precipitation of pure *mer*-$[IrH_3(PPh_3)_3]$. After cooling and concentrating the filtrate other products, including *fac*-$[IrH_3(PPh_3)_3]$, were deposited. With 2-methoxyethanol as solvent this reaction gave a mixture of *mer*- and *fac*-$[IrH_3(PPh_3)_3]$, which was identified by i.r. spectroscopy. Sodium borohydride reduction of osmium salts in the presence of triphenylphosphine gave modest yields of $[OsH_4(PPh_3)_3]$ as rather inert, insoluble, white microcrystals. The low solubility of osmium salts in alcoholic solvents necessitated their use in the form of finely divided alcoholic suspensions. The osmium hydride preparation is not a particularly satisfactory one, but it is the only route currently available to this interesting compound. The n.m.r. spectrum of $[OsH_4(PPh_3)_3]$ shows a 1 : 3 : 3 : 1 quartet (J_{PH} 9 Hz) at τ 17·85 (relative intensity 4) as the only high field signal, thus suggesting that all four hydride ligands are magnetically equivalent and couple equally with the three ^{31}P nuclei present. An impure sample of $[OsH_4(AsPh_3)_3]$, prepared in our laboratory, showed a single sharp line in the high field n.m.r. spectrum, thus confirming our assignment of the 1 : 3 : 3 : 1 quartet observed for $[OsH_4(PPh_3)_3]$. The osmium tetrahydrides, other examples of which have been discussed recently elsewhere,[18] are members of a series of transition-metal multihydride complexes $[MH_x(PR_3)_3]$ in which all the hydride ligands are magnetically equivalent and couple equally with all ^{31}P nuclei present in the molecule.[18,19] Other examples include $[WH_6(PMe_2Ph)_3]$,[20] $[ReH_5(PPh_3)_3]$,[21] both of which show a similar 1 : 3 : 3 : 1 quartet pattern in the high field n.m.r. spectrum.

Carbonyl and Hydridocarbonyl Complexes.—Many phosphine complexes of the platinum metals slowly abstract carbon monoxide or hydrogen from boiling alcoholic solvents, particularly in the presence of base, to yield carbonyl or hydride derivatives, respectively.[22] However, in the hydride syntheses described above, side reactions involving decarbonylation on the alcoholic

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solvent are prevented by the very rapid precipitation and removal of the required platinum metal hydrides which are thus obtained free from carbonyl ligands. Modification of these reactions to permit carbonyl formation is readily achieved by introduction of aqueous formaldehyde solution, a common source of carbonyl ligands,[23] thus providing convenient syntheses of $[RhH(CO)(PPh_3)_3]$ and a wide range of iridium and ruthenium carbonyl or hydridocarbonyl derivatives.

Preparations of $[RhH(CO)(PPh_3)_3]$ reported in the literature are based on the synthesis of $[RhCl(CO)(PPh_3)_2]$ and its subsequent reduction with hydrazine,[24] sodium borohydride,[25] or triethylamine and hydrogen,[25] in the presence of excess of triphenylphosphine, to yield the required complex. The present method is essentially similar to one recently reported by Wilkinson [26] and permits the synthesis of $[RhH(CO)(PPh_3)_3]$ from rhodium trichloride in a single reaction. The experimental details correspond to those used in the synthesis of $[RhH(PPh_3)_4]$, except that aqueous formaldehyde is added to the reaction solution prior to the sodium borohydride and a longer reaction time is allowed to ensure complete conversion of the very insoluble $[RhCl(CO)(PPh_3)_2]$ which tends to precipitate from the reaction mixture. The related iridium(I) complex $[IrH(CO)(PPh_3)_3]$ may be conveniently prepared by a similar one stage reaction conducted in boiling 2-methoxyethanol solution; the required product crystallises directly and in good yield when the reaction mixture is cooled and diluted with methanol. This synthesis is rapid and much more convenient than the multistage syntheses given in the literature.[24,27,28] Several other important iridium complexes can be obtained in good yield by minor modifications of the above reaction. Thus, addition of sodium chloroiridate and aqueous formaldehyde to a boiling solution of 2-methoxyethanol containing a small excess of triphenylphosphine leads to rapid precipitation of pure $[IrCl_2H(CO)(PPh_3)_2]$.[29] The same reaction performed in the presence of a two-fold excess of triphenylphosphine gives α-$[IrCl_2H(PPh_3)_3]$.[30] In this latter reaction, the excess of phosphine presumably competes successfully with the formaldehyde for co-ordination sites on the iridium and thus suppresses the carbonylation process. The synthesis of $[IrCl_2H(CO)(PPh_3)_2]$ may be modified to yield pure $[IrCl(CO)(PPh_3)_2]$ by addition of neat triethylamine to the reaction mixture and slightly extending the reaction time. The triethylamine removes hydrogen chloride from the $[IrCl_2H(CO)(PPh_3)_2]$ formed in the reaction.[31] This synthesis clearly has advantages over literature methods involving the use of carbon monoxide [32] or dimethylformamide, high temperatures, and prolonged reaction times.[33] Attempts to form the bromo-derivatives $[IrBr_2H(CO)(PPh_3)_2]$ and $[IrBr_2H(PPh_3)_3]$ by use of sodium bromoiridate in the above reactions gave complex mixtures of products. However, attempted synthesis of $[IrBr(CO)(PPh_3)_2]$ by introduction of triethylamine to the appropriate reaction mixture gave instead good yields of $[IrH(CO)(PPh_3)_3]$. Precipitation of this latter product suggests the intermediate formation of $[IrBr(CO)(PPh_3)_2]$ with subsequent conversion to hydride by the alcoholic triethylamine solution: a similar process occurs for the chloride analogue if the reaction time is prolonged.

Closely related reactions involving ' hydrated ruthenium trichloride ' provide convenient syntheses of the known complexes $[RuClH(CO)(PPh_3)_3]$, $[RuH_2(CO)(PPh_3)_3]$ (white isomer), and $[Ru(CO)_3(PPh_3)_2]$ in good yield. $[RuClH(CO)(PPh_3)_3]$ has hitherto been prepared by prolonged reaction of ruthenium trichloride and triphenylphosphine in basic alcoholic media.[34,35] The literature synthesis of $[RuH_2(CO)(PPh_3)_3]$ (white isomer) involves the prolonged sodium borohydride reduction of $[RuCl_2(PPh_3)_3]$ in boiling ethanol, under an atmosphere of hydrogen.[14] The ruthenium(0) complex $[Ru(CO)_3(PPh_3)_2]$ is an important precursor for a range of ruthenium species and several methods of synthesis are available; these include reaction of $Ru(CO)_5$ [36] or $Ru_3(CO)_{12}$ [37] with triphenylphosphine, zinc dust reduction of $[RuCl_2(CO)_2(PPh_3)_2]$ in the presence of carbon monoxide,[38] and the reaction of $[RuH(OAc)(PPh_3)_3]$ with carbon monoxide.[39] The new syntheses described below offer several advantages over these established methods of preparation.

Addition of hydrated ruthenium trichloride and aqueous formaldehyde to triphenylphosphine in 2-methoxyethanol under reflux gives rapid precipitation of $[RuClH(CO)(PPh_3)_3]$ in excellent yield; the same reaction is less satisfactory in boiling ethanol. When solutions of hydrated ruthenium trichloride, formaldehyde, and sodium borohydride are added rapidly and successively to triphenylphosphine in boiling ethanol, rapid precipitation of $[RuH_2(CO)(PPh_3)_3]$ (white isomer)

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occurs while a similar reaction in boiling 2-methoxyethanol gives [$Ru(CO)_3(PPh_3)_2$] in 63% yield. In this latter reaction, intermediate formation of [$RuH_2(CO)_2(PPh_3)_2$] (ν_{CO} 2011 and 1974; ν_{RuH} 1878 and 1823 cm^{-1}) [36] was observed but we were unable to isolate the pure complex. Attempts to prepare ruthenium(0) carbonyl derivatives by addition of triethylamine and excess of triphenylphosphine in the preparation of [$RuClH(CO)(PPh_3)_3$] gave only [$RuH_2(CO)(PPh_3)_3$] in modest yield.

Our efforts to devise convenient syntheses of osmium carbonyl and hydridocarbonyl complexes were frustrated by precipitation of mixed products.

Nitrosyl Complexes.—Nitrosyl-containing triphenylphosphine complexes of the platinum metals have previously been prepared by reactions involving use of nitric oxide or nitrosyl halides,[40] and the reaction of metal hydride complexes with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide has also been employed.[40,41] The new preparations are based on the use of this latter reagent but do not require isolation of the intermediate hydride and thus permit a high degree of efficiency and flexibility. We have chosen *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in preference to other *N*-nitroso compounds as the source of nitrosyl ligands because it is a stable crystalline solid, readily available commercially and, unlike many other *N*-nitroso compounds, free from carcinogenic properties.[42] Complexes prepared by this new technique comprise [$MCl_2(NO)(PPh_3)_2$] (M = Rh and Ir); [$MCl_3(NO)(PPh_3)_2$] (M = Ru and Os); [$Rh(NO)(PPh_3)_3$] and [$Ru(NO)_2(PPh_3)_2$].

The nitrosyl complexes [$RhCl_2(NO)(PPh_3)_2$] [43] and [$RuCl_3(NO)(PPh_3)_2$] [44] are usually prepared by treatment of the nitrosyls [$RhCl(NO)_2]_n$ and [$RuCl_3(NO)]_n$ respectively, with triphenylphosphine. The iridium(I) nitrosyl [$IrCl_2(NO)(PPh_3)_2$] has been synthesised by treatment of [$Ir(NO)_2(PPh_3)_2]^+ClO_4^-$ (ref. 45) or [$Ir(NO)(PPh_3)_3$] [46] with hydrogen chloride. The related osmium(II) nitrosyl [$OsCl_3(NO)(PPh_3)_2$] has recently been obtained by a multistage synthesis.[47] The preparation has recently been reported of the complexes [$RhCl_2(NO)(PPh_3)_2$],[48] [$IrCl_2(NO)(PPh_3)_2$],[48] and [$OsCl_3(NO)(PPh_3)_2$] [49] by reaction of [$RhCl_2(NO)]_n$, [$IrCl_2(NO)(C_8H_{12})$], and $Na_2[OsCl_6]$ and NO respectively with PPh_3.

We now find that addition of alcoholic solutions of the appropriate metal chloride or chloro-complex and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide to a boiling alcoholic solution of triphenylphosphine gives rapid precipitation of the desired nitrosyl chloride complex in good yield. The rhodium and ruthenium derivatives are prepared with ethanolic solutions while the iridium and osmium complexes require use of the higher boiling solvent, 2-methoxyethanol. The ruthenium and osmium nitrosyls prepared in this manner show an additional band in their i.r. spectra, possibly due to a second nitrosyl derivative. This impurity may be removed by dissolving the complexes in boiling chloroform, in which they are sparingly soluble, and reprecipitating them with cold methanol. The rhodium and iridium nitrosyls are precipitated in an essentially pure state. The formation of these nitrosyls probably involves the transient existence in solution of the hydride derivatives [$MHCl_2(PPh_3)_3$] (M = Rh and Ir) or [$MHCl_3(PPh_3)_2$] (M = Ru and Os) which subsequently react with *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide in the usual manner. Rhodium(III) [50] and iridium(III) [30] monohydride complexes of this type form under conditions similar to those employed here and the formation of related ruthenium(IV) and osmium(IV) monohydrides appears entirely feasible. The extension of the syntheses to include related nitrosyl complexes containing other anionic and neutral ligands is in progress and will be reported elsewhere.

Modification of the rhodium and ruthenium nitrosyl preparations by rapid introduction of sodium borohydride leads to precipitation of the halide free nitrosyl derivatives [$Rh(NO)(PPh_3)_3$] and [$Ru(NO)_2(PPh_3)_2$], respectively. Care is needed in these preparations to avoid contamination of the products with halide-containing species, but if this does occur, further purification can be readily effected. The rhodium complex [$Rh(NO)(PPh_3)_3$] has previously been prepared by sodium amalgam reduction of a mixture of rhodium nitrosyl chloride and triphenylphosphine in tetrahydrofuran.[43] Preparations from [$RhH(PPh_3)_4$] and nitric oxide [12] and from rhodium trichloride, nitric oxide, triphenylphosphine, and zinc dust [51] have also been effected. The complex [$Ru(NO)_2(PPh_3)_2$] was the first well defined ruthenium dinitrosyl to be reported.[2] No evidence of nitrosyl formation was found on reacting *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide with platinum or palladium salts and triphenylphosphine. This observation possibly reflects the tendency of these metals to form zero oxidation-state complexes in preference to hydrides.

EXPERIMENTAL *

Microanalyses were performed by Dr. Strauss (formerly with Dr. Weiler), at Oxford and by Dr. Bernhardt, Mulheim,

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* *Note added in proof:* More recent studies (with M. F. Uttley) show that $NaBH_4$ may be replaced in some of these reactions by an equimolar quantity of potassium hydroxide. The use of this latter reagent is particularly advantageous in preparations of the rhodium complexes [$RhH(PPh_3)_4$] and [$Rh(NO)(PPh_3)_3$].

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Germany. I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 457 grating spectrometer unless otherwise stated. N.m.r. spectra were obtained with a Perkin-Elmer R10 instrument. Platinum metal salts were purchased from Johnson Matthey; hydrated ruthenium trichloride was used as purchased and may have contained appreciable amounts of ruthenium(IV) species. Triphenylphosphine, *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide, 40% aqueous formaldehyde, and sodium borohydride were purchased from B.D.H. and used without further purification.

All reactions were performed under oxygen-free nitrogen.

Preparation of Hydride-, Carbonyl-, and Nitrosyl-containing Complexes of the Platinum Metals. General Observations.—The success of the following preparations depends upon the maintenance of essentially homogeneous conditions until the reactions are complete. This requires the addition of the various reagent solutions *rapidly* and *successively* to the vigorously boiling reaction mixture, and failure to observe this precaution leads to precipitation of insoluble intermediates which may fail to react further, and thus contaminate the product. The reactions are conveniently performed in a conical flask (100—250 ml) fitted with a condenser, a nitrogen inlet, and a port for introduction of reagent solutions. The reaction solutions were stirred magnetically. The products were frequently deposited in a pure state; further purification was achieved where necessary by application of literature methods. The use of these reactions for large scale syntheses has not been investigated, and difficulties in achieving homogeneous solutions may be encountered under these conditions.

Rhodium Complexes.—*Hydridotetrakis*(*triphenylphosphine*)*rhodium.* Hydrated rhodium trichloride (0·13 g, 0·5 mmol) in warm ethanol (10 ml) and sodium borohydride (0·10 g, 2·5 mmol) in warm ethanol (10 ml) were added rapidly and successively to a vigorously stirred solution of triphenylphosphine (1·31 g, 5·0 mmol) in boiling ethanol (40 ml). The mixture was heated under reflux for *ca.* 5 min to ensure complete reaction, then cooled to 30°, filtered, and the precipitate washed with water, ethanol, and n-hexane to give the *product* as orange-brown microcrystals (0·55 g, 95%) ν_{RhH} 2140 cm^{-1} (lit.,[10] 2140 cm^{-1}) (Found: C, 74·6; H, 5·5; Cl, 0·0; P, 10·5. Calc. for $C_{72}H_{61}P_4Rh$: C, 75·0; H, 5·35; Cl, 0·0; P, 10·75%). With a smaller amount of triphenylphosphine (0·65 g, 2·5 mmol) an orange-red compound (0·34 g) was deposited. This product was probably [$RhH(PPh_3)_3$] but was not investigated further.

Hydridocarbonyltris(*triphenylphosphine*)*rhodium.* Hydrated rhodium trichloride (0·13 g) in ethanol (10 ml), aqueous formaldehyde (5 ml), and sodium borohydride (0·10 g) in ethanol (10 ml) were added in rapid succession to a stirred solution of triphenylphosphine (1·31 g) in boiling ethanol (40 ml). After 15 min more ethanolic sodium borohydride solution (0·10 g in 10 ml) was added and the mixture was heated under reflux for a further 15 min. The mixture was cooled, filtered, and the precipitate washed with water, ethanol, and n-hexane to give the *product* as yellow microcrystals (0·435 g, 95%), ν_{CO} 1915, ν_{RhH} 2030 cm^{-1} (lit.,[26] ν_{CO} 1920, ν_{RhH} 2040 cm^{-1}).

Nitrosyltris(*triphenylphosphine*)*rhodium.* Hydrated rhodium trichloride (0·13 g) in ethanol (10 ml), *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·21 g, 1·0 mmol) in ethanol (10 ml), and sodium borohydride (0·10 g) in ethanol (10 ml) were added in rapid succession to a well stirred solution of triphenylphosphine (1·31 g) in boiling ethanol (40 ml). The mixture was heated under reflux for 10 min and then cooled to 30° and filtered; the precipitate was washed successively with ethanol, water, and ethanol and then dried *in vacuo* to give the product as orange-red *microcrystals* (0·40 g, 87%), ν_{NO} 1610 cm^{-1} (lit.,[12] ν_{NO} 1610 cm^{-1}) (Found: C, 70·6; H, 5·05; N, 1·7. Calc. for $C_{54}H_{45}NOP_3Rh$: C, 70·5; H, 4·85; N, 1·5%).

Dichloronitrosylbis(*triphenylphosphine*)*rhodium.* Reagents and conditions were analogous to those for preparation of nitrosyltris(triphenylphosphine)rhodium, but the addition of sodium borohydride solution was omitted. The resultant mixture was heated under reflux for *ca.* 2 min and the precipitate was filtered off washed with ethanol, and dried *in vacuo* to give the product as light brown *platelets* (0·27 g, 74%) ν_{NO} 1630 cm^{-1} (lit.,[48] ν_{NO} 1632 cm^{-1}) (Found: C, 59·35; H, 4·1; N, 2·2. Calc. for $C_{36}H_{30}Cl_2NOP_2Rh$: C, 59·3; H, 4·15; N, 1·9%).

Iridium Complexes.—mer-*Trihydridotris*(*triphenylphosphine*)*iridium.* Sodium chloroiridate (0·28 g, 0·5 mmol) was digested with warm ethanol for 10 min. The filtered extract and sodium borohydride (0·10 g) in ethanol (10 ml) were added successively to triphenylphosphine (1·05 g, 4·0 mmol) in ethanol (40 ml) heated under reflux. The mixture was heated for a further 15 min, cooled to *ca.* 50°, filtered, and the resultant precipitate was washed with water and methanol to give the product as white *microcrystals* (0·20 g, 41%), ν_{IrH} 1740 and 2130 cm^{-1} (lit.,[16] ν_{IrH} 1750 and 2130 cm^{-1}) (Found: Cl, 0·0. $C_{54}H_{48}IrP_3$ requires Cl, 0·0%).

The filtrate from this reaction was cooled and concentrated *in vacuo* and other products including appreciable quantities of *fac*-[$IrH_3(PPh_3)_3$] were deposited.

Hydridocarbonyltris(*triphenylphosphine*)*iridium.* Sodium chloroiridate (0·28 g) in 2-methoxyethanol (10 ml), aqueous formaldehyde (5 ml), and sodium borohydride (0·1 g) in 2-methoxyethanol (10 ml) were added in rapid succession to a vigorously stirred solution of triphenylphosphine (0·79 g) in boiling 2-methoxyethanol (30 ml). The mixture was heated under reflux for 15 min, cooled, and then diluted with methanol (20 ml); the resultant crystals were filtered off, washed with water, ethanol, and diethyl ether and then dried *in vacuo* to give the product as yellow *needles* (0·45 g, 90%), ν_{CO} 1915, ν_{IrH} 2120 cm^{-1}, τ (C_6H_6) 20·3 (quartet, *J* 21·3 Hz) * (Found: C, 65·55; H, 4·7. Calc. for $C_{55}H_{46}IrOP_3$: C, 65·8; H, 4·6%).

Chlorocarbonylbis(*triphenylphosphine*)*iridium.* Sodium chloroiridate (0·28 g) in 2-methoxyethanol (10 ml) was added to a boiling solution of triphenylphosphine (0·39 g, 1·5 mmol) in 2-methoxyethanol (25 ml). Aqueous formaldehyde (5 ml) and triethylamine (5 ml) were introduced and the mixture was heated under reflux for 10 min. The mixture was then cooled, and diluted with methanol (35 ml); the precipitate was filtered off, washed with water, methanol, and diethyl ether to give the product as yellow *microcrystals* (0·23 g, 58%), ν_{CO} 1950 cm^{-1} (lit.,[33] 1961 cm^{-1}) (Found: C, 57·4; H, 3·85. Calc. for $C_{37}H_{30}ClIrOP_2$: C, 56·95; H, 3·9%).

Dichlorohydridocarbonylbis(*triphenylphosphine*)*iridium.* Sodium chloroiridate (0·28 g) in 2-methoxyethanol (10 ml)

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* Spectroscopic data recorded in the literature[52] for the complex [$IrH(CO)(PPh_3)_3$] appear to be in error. The results which we record were obtained on samples prepared by the new technique and were confirmed with an authentic specimen prepared by the original method.

[52] A. P. Ginsberg, 'Transition Metal Chemistry,' 1965, **1**, 111, and references therein.

and aqueous formaldehyde (10 ml) were added successively to a stirred solution of triphenylphosphine (0·39 g) in boiling 2-methoxyethanol. The mixture was boiled for *ca.* 15 min, cooled, and the white complex was filtered off, washed successively with water, methanol, and diethyl ether then dried *in vacuo* (0·39 g, 95%), ν_{CO} 2020, ν_{IrH} 2230 cm^{-1} (lit.,[29] ν_{CO} 2030, ν_{IrH} 2245 cm^{-1}) (Found: C, 54·35; H, 4·05. Calc. for $C_{37}H_{31}Cl_2IrOP_2$: C, 54·4; H, 3·85%). Attempts to prepare dibromohydridocarbonylbis(triphenylphosphine)-iridium by a similar reaction involving the use of sodium bromoiridate gave an unidentified pale yellow complex (0·18 g) (ν 2195w cm^{-1}).

Dichlorohydridotris(triphenylphosphine)iridium.— Sodium chloroiridate (0·28 g) in 2-methoxyethanol (10 ml) and aqueous formaldehyde (5 ml) were added successively to a stirred solution of triphenylphosphine (0·78 g) in boiling 2-methoxyethanol (25 ml). The mixture was boiled for *ca.*, 2 min, cooled, diluted with methanol, and the product isolated as *yellow microcrystals* (0·33 g, 65%) ν_{IrH} 2197 cm^{-1} (lit.,[53] 2197 cm^{-1}) (Found: C, 62·3; H, 4·8. Calc. for $C_{44}H_{46}Cl_2IrP_3$: C, 61·8; H, 4·4%).

Attempted preparation of bromocarbonylbis(triphenylphosphine)iridium: a second route to hydridocarbonyltris(triphenylphosphine)iridium. Sodium bromoiridate (0·356 g) in 2-methoxyethanol (10 ml) was added to a boiling solution of triphenyiphosphine (0·39 g) in 2-methoxyethanol (25 ml). Aqueous formaldehyde (5 ml) and neat triethylamine (5 ml) were introduced and the mixture was heated under reflux for 15 min. The mixture was then cooled and diluted with methanol (35 ml); the resultant precipitate was filtered off and washed with water to give hydridocarbonyltris(triphenylphosphine)iridium (0·19 g, 45%) (from benzene–methanol), ν_{CO} 1930, ν_{IrH} 2120 cm^{-1} (Found: C, 65·7; H, 4·75. Calc. for $C_{55}H_{46}IrOP_3$: C, 65·8; H, 4·6%).

Dichloronitrosylbis(triphenylphosphine)iridium. Sodium chloroiridate (0·28 g) in 2-methoxyethanol (10 ml) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·21 g) in 2-methoxyethanol (10 ml) were added successively to a stirred solution of triphenylphosphine (0·79 g) in boiling 2-methoxyethanol (20 ml). The mixture was boiled for 15 min and then the light brown precipitate was filtered off and washed with water, ethanol, and diethyl ether to give the product as orange brown *microcrystals* (0·21 g, 52%), ν_{NO} 1560 cm^{-1} (lit.,[45] 1560 cm^{-1}) (Found: C, 53·15; H, 3·9; N, 1·8. Calc. for $C_{36}H_{30}Cl_2IrNOP_2$: C, 52·9; H, 3·7; N, 1·7%).

Ruthenium Complexes.—Dihydridotetrakis(triphenylphosphine)ruthenium. Hydrated ruthenium trichloride (0·53 g, 2·0 mmol) in hot ethanol (20 ml) was added rapidly to a vigorously stirred solution of triphenylphosphine (3·14 g, 12·0 mmol) in boiling ethanol (120 ml). Subsequent, rapid, portionwise addition of sodium borohydride (0·38 g, 10·0 mmol) in hot ethanol (20 ml) gave a yellow precipitate which was filtered off, washed with ethanol, water, and ethanol, and dried *in vacuo* to give the product as mustard yellow *microcrystals* (2·17 g, 94%), ν_{RuH} 2080 cm^{-1} (lit.,[7] 2080 cm^{-1}) (Found: C, 74·6; H, 5·8; Cl, 0·0. Calc. for $C_{72}H_{62}P_4Ru$: C, 75·05; H, 5·45; Cl, 0·0%).

Dihydridotris(triphenylphosphine)ruthenium (?) A complex of this apparent formula was obtained as a brown microcrystalline *powder* (1·62 g, 92%) in the above reaction when a reduced quantity of triphenylphosphine (1·57 g, 6·0 mmol) was used (Found: C, 73·2; H, 5·65. $C_{54}H_{47}P_3Ru$ requires: C, 72·9; H, 5·35%), ν_{RuH} 1890 and 1960 cm^{-1}, τ (benzene, under argon) 27·2 (1 : 3 : 3 : 1 q, J_{PH} 28 Hz).

Conversion of dihydridotris(triphenylphosphine)ruthenium into dihydridotetrakis(triphenylphosphine)ruthenium. A suspension of crushed dihydridotris(triphenylphosphine)ruthenium (0·10 g) and triphenylphosphine (0·10 g) in ethanol (20 ml) was heated under reflux for 30 min and then cooled. The complex was filtered off, washed with methanol, and dried *in vacuo* to give the product (0·09 g) which was identical with an authentic specimen.

Conversion of dihydridotris(triphenylphosphine)ruthenium into dihydridocarbonyltris(triphenylphosphine)ruthenium. A stirred suspension of dihydridotris(triphenylphosphine)-ruthenium (0·25 g) in methanol (25 ml) was heated under reflux with aqueous formaldehyde (2·5 ml) for 1 h. The resultant precipitate was filtered off and washed with methanol to give the product (0·24 g) which was identical with an authentic specimen.

Conversion of dihydridotris(triphenylphosphine)ruthenium into dinitrosylbis(triphenylphosphine)ruthenium. A finely divided suspension of dihydridotris(triphenylphosphine)-ruthenium (0·10 g) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·10 g) in methanol (15 ml) was gently warmed until dark red crystals formed (*ca.* 5 min). The complex (0·05 g, 65%), identical with an authentic sample (see below), was filtered off, washed with methanol, and dried *in vacuo*.

Dihydridocarbonyltris(triphenylphosphine)ruthenium. Hydrated ruthenium trichloride (0·26 g) in ethanol (10 ml), aqueous formaldehyde (10 ml), and sodium borohydride (0·19 g) in ethanol (10 ml) were added in rapid succession to a stirred solution of triphenylphosphine (1·57 g, 6·0 mmol) in boiling ethanol (70 ml). The mixture was heated under reflux for 15 min, and then cooled; the resultant precipitate was filtered off, washed with ethanol, water, and ethanol, and dried *in vacuo*. Recrystallisation from benzene–light petroleum (b.p. 40—60°) gave the product as white *microcrystals* (0·69 g, 75%), ν_{CO} 1940, ν_{RuH} 1960 and 1900 cm^{-1} (lit.,[14] ν_{CO} 1940, ν_{RuH} 1960 and 1900 cm^{-1}) (Found: C, 71·8; H, 5·2; P. 9·7. Calc. for $C_{55}H_{47}OP_3Ru$: C, 71·7; H, 5·0; P, 10·1%). Recrystallisation from dichloromethane–methanol gave a dichloromethane adduct $[RuH_2(CO)(PPh_3)_3CH_2Cl_2]$ (Found: C, 67·0; H, 4·9; Cl, 6·9. $C_{56}H_{49}Cl_2OP_3Ru$ requires C, 67·0; H, 4·9; Cl, 7·05%).

Tricarbonylbis(triphenylphosphine)ruthenium. Hydrated ruthenium trichloride (0·13 g) in 2-methoxyethanol (10 ml), aqueous formaldehyde (10 ml), and sodium borohydride (0·10 g) in 2-methoxyethanol (10 ml) were added successively to a solution of triphenylphosphine (0·79 g) in boiling 2-methoxyethanol (30 ml). The mixture was heated under reflux for 1 h and cooled; the resultant precipitate was filtered off, washed with water and ethanol, and then dried *in vacuo* to give the product as cream *microcrystals* (0·225 g, 63%), ν_{CO} 1900 cm^{-1} (lit.,[36] 1900 cm^{-1}) (Found: C, 66·0; H, 4·2. Calc. for $C_{39}H_{30}P_2O_3Ru$: C, 66·0; H, 4·25%).

Chlorohydridocarbonyltris(triphenylphosphine)ruthenium. This was obtained after 5 min from the previous reaction when the sodium borohydride addition was omitted (yield 0·78 g, 82%), ν_{CO}, ν_{RuH} 2010, 1920, and 1900 cm^{-1} (lit.,[34] 2017, 1924, and 1903 cm^{-1}) (Found: C, 69·5; H, 4·84; Cl, 4·2. Calc. for $C_{55}H_{46}ClOP_3Ru$: C, 69·35; H, 4·85; Cl, 3·8%).

Dinitrosylbis(triphenylphosphine)ruthenium. Hydrated

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[53] L. Vaska and J. W. DiLuzio, *J. Amer. Chem. Soc.*, 1962, **84**, 4989.

ruthenium trichloride (0·13 g) in ethanol (10 ml) was added rapidly to a stirred solution of triphenylphosphine (0·79 g) in boiling ethanol (40 ml). Sodium borohydride (0·1 g) in ethanol (10 ml) was then added dropwise until a deep purple colour developed. *N*-Methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·21 g) in ethanol and the remaining sodium borohydride solution were rapidly added. The mixture was heated for *ca.* 5 min and then cooled; the resultant precipitate was filtered off, washed with ethanol, water, and ethanol, and then dried *in vacuo* to give the product as dark red *needles* (0·275 g, 82%), ν_{NO} 1665 and 1619 cm^{-1} (CH_2Cl_2 solution) (Found: C, 58·05; H, 4·75; N, 3·85. $C_{36}H_{30}N_2O_2P_2Ru$ required C, 58·25; H, 4·90; N, 3·25%).

Trichloronitrosylbis(*triphenylphosphine*)*ruthenium*. Hydrated ruthenium trichloride (0·13 g) in ethanol (10 ml) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·21 g) in ethanol (10 ml) were added rapidly to a solution of triphenylphosphine (0·79 g) in boiling ethanol (20 ml). The mixture was boiled for *ca.* 2 min and then cooled and filtered; the precipitate was washed with ethanol to give the impure complex as green platelets (ν_{NO} 1870vs and 1740w cm^{-1}). Recrystallisation from dichloromethane–methanol gave the pure product as orange *microcrystals* (yield 0·25 g, 69%), ν_{NO} 1870 cm^{-1} (lit.,[44] 1870 cm^{-1}) (Found: C, 56·2; H, 4·1. Calc. for $C_{36}H_{30}Cl_3NORu$: C, 56·8; H, 4·0%).

Osmium Complexes.—*Tetrahydridotris*(*triphenylphosphine*)*osmium*. Method 1. Sodium chloro-osmate (0·28 g, 0·5 mmol) was extracted with cold ethanol (10 ml). The filtered extract and sodium borohydride (0·10 g, 2·5 mmol) in ethanol (10 ml) were added successively to a vigorously stirred solution of triphenylphosphine (0·66 g, 2·5 mmol) in boiling ethanol (40 ml). The mixture was stirred and heated under reflux for *ca.* 15 min, and then cooled; the resultant precipitate was washed thoroughly with water and ethanol and then dried *in vacuo* (0·18 g, 38%), ν_{OsH} 2080w, 2020m, and 1890s cm^{-1} (Found: C, 66·25; H, 5·5; Cl, 0·0. $C_{54}H_{49}OsP_3$ requires C, 66·1; H, 5·05; Cl, 0·0; P, 9·45%).

Method 2. Sodium borohydride (0·10 g) in warm ethanol (10 ml) was added during 3 min to a vigorously stirred suspension of ammonium bromo-osmate (0·36 g, 0·5 mmol) and triphenylphosphine (0·66 g) in boiling ethanol (50 ml). The mixture was heated under reflux for 5 min and then cooled; the resultant precipitate was recrystallised from dichloromethane–methanol to give the product (Found: C, 66·3; H, 5·5; P, 9·8; Br, 0·0%).

Trichloronitrosylbis(*triphenylphosphine*)*osmium*. Sodium chloro-osmate (0·28 g) in 2-methoxyethanol (10 ml) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·21 g) in 2-methoxyethanol (10 ml) were added successively to a boiling solution of triphenylphosphine (0·79 g) in 2-methoxyethanol (20 ml). The mixture was heated under reflux for 10 min and then cooled; the precipitate was filtered off, washed with water and ethanol, and then dried *in vacuo* to give the product as orange microcrystals (0·22 g, 52%), ν_{NO} 1848 (lit.,[47] 1850 cm^{-1}) (Found: C, 51·2; H, 3·7; N, 1·7. $C_{36}H_{30}Cl_3NOOsP_2$ requires C, 50·85; H, 3·55; N, 1·65%).

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