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Complexes of the Platinum Metals. Part XIX [1]. Convenient Syntheses of some Triphenylarsine Derivatives containing Hydride and/or Carbonyl Ligands

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The complexes $[MCl_2(CO)(AsPh_3)_3]$ (M = Ru or Os) have been prepared by addition of $RuCl_3 \cdot 3H_2O$ or $Na_2OsCl_6 \cdot 6H_2O$ and aqueous formaldehyde to excess triphenylarsine in boiling 2-methoxyethanol. Similar reactions, modified by addition of triethylamine, afford the corresponding hydrides $[MHCl(CO)(AsPh_3)_3]$. In boiling toluene the complexes $[MCl_2(CO)(AsPh_3)_3]$ readily eliminate triphenylarsine to form binuclear complexes $[M_2Cl_4(CO)_2(AsPh_3)_4]$. Carbonylation of the complexes $[MCl_2(CO)(AsPh_3)_3]$ and $[MHCl(CO)(AsPh_3)_3]$ in boiling benzene affords the dicarbonyls $[MCl_2(CO)_2(AsPh_3)_2]$ and $[MHCl(CO)_2(AsPh_3)_2]$ respectively. Reduction of the complexes $[MCl_2(CO)(AsPh_3)_3]$ with sodium borohydride in ethanol yields the corresponding dihydrides $[MH_2(CO)(AsPh_3)_3]$. The tetrahydride $[OsH_4(AsPh_3)_3]$ is readily prepared from $Na_2OsCl_6 \cdot 6H_2O$, triphenylarsine and sodium borohydride in ethanol, the facial isomer of $[IrH_3(AsPh_3)_3]$ is similarly obtained from $Na_2IrCl_6 \cdot 6H_2O$. By careful adjustment of pH and chloride ion concentration the reaction of $Na_2IrCl_6 \cdot 6H_2O$ with triphenylarsine in boiling 2-methoxyethanol can be made to yield $[IrH_2Cl(AsPh_3)_3]$, $[IrHCl_2(AsPh_3)_3]$ or $[IrCl_3(AsPh_3)_3]$. Attempts to prepare a range of other platinum metal triphenylarsine complexes are described. The new complexes have been characterised by elemental analysis, melting point and spectroscopic data.

Introduction

Some years ago we reported convenient, single stage syntheses for a range of platinum group metal triphenylphosphine complexes containing hydride, carbonyl or nitrosyl ligands [2–4]. In the intervening years these syntheses have been widely adopted in other laboratories, and have greatly improved the accessibility of the complexes concerned. The object of the present exercise was to develop a parallel series of syntheses using triphenylarsine in place of triphenylphosphine. Unfortunately the poorer ligand properties [5–7] of the arsine relative to the phosphine have largely negated our efforts and only modest success has been achieved. However, the results discussed below include the preparation of several new triphenylarsine complexes, and improved syntheses for a number of others. In the absence of a suitable arsenic isotope the amount of information which can be gleaned by NMR spectroscopy is very limited and stereochemical assignments are correspondingly difficult to achieve for triphenylarsine complexes. However, using ^1H NMR data we have been able to make unambiguous stereochemical assignments for several new and some previously reported complexes.

Experimental

Platinum group metal salts, $RuCl_3 \cdot 3H_2O$ (39% Ru), $Na_2OsCl_6 \cdot 6H_2O$ (34% Os), $RhCl_3 \cdot 3H_2O$ (39% Rh), and $Na_2IrCl_6 \cdot 6H_2O$ (34% Ir) were supplied by Johnson Matthey Chemicals Ltd. The reagent grade solvents, ethanol, 2-methoxyethanol and toluene were used as purchased. Single stage syntheses based on use of platinum metal chlorides or chloro complexes were performed using the special apparatus and conditions previously described [3]. The products were washed successively with methanol (2 × 10 ml), water (2 × 10 ml) methanol (2 × 10 ml) and n-hexane (10 ml) then dried *in vacuo*.

Elemental analyses were performed by the University of London School of Pharmacy Laboratories. Melting points were determined on a Buchi capillary melting point apparatus using samples sealed under nitrogen. Unless otherwise indicated infrared spectra were run as Nujol mulls on a Perkin-Elmer 457 grating spectrometer. Proton NMR were obtained at 90 MHz using a Bruker HFX90/NMR spectrometer

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operating in Fourier transform mode. All were run with TMS used as an internal standard in deuteriochloroform as solvent unless otherwise indicated.

Dichlorocarbonyltris(triphenylarsine)ruthenium(II)

Solutions of hydrated ruthenium trichloride (0.295 g, 1.13 mmol) in 2-methoxyethanol (20 ml) and aqueous formaldehyde (22 ml, 40% solution) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylarsine (1.85 g, 6.05 mmol) in 2-methoxyethanol (60 ml). The mixture was heated under reflux for 2 hours during which time the solution became pale orange. After cooling, the solution was reduced to 50 ml volume then diluted with cold methanol (50 ml). The yellow precipitate which formed was separated and washed as in the general experimental procedure to afford the required product as yellow microcrystals, 1.06 g (83%). M. pt. 186 °C. Infrared, ν(CO) 1948(s), 1912(m) cm^{-1}. *Anal.* Calcd. for $C_{55}H_{45}As_3Cl_2ORu$: C, 59.04; H, 4.06%. Found: C, 58.20; H, 4.18%.

Dichlorocarbonyltris(triphenylarsine)osmium(II)

Solutions of sodium hexachloroosmate hexahydrate (0.678 g, 1.21 mmol) in 2-methoxyethanol (35 ml) and aqueous formaldehyde (17.5 ml, 40% solution) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylarsine (2.41 g, 7.86 mmol) in 2-methoxyethanol (75 ml). The mixture was heated under reflux for one hour then allowed to cool to room temperature. The orange precipitate was filtered off and washed as in the general experimental procedure to yield the required product as orange microcrystals, 1.28 g (86%). M. pt. 251 °C. Infrared, ν(CO) 1920(vs), 1910(s), 1891(w) cm^{-1}. *Anal.* Calcd. for $C_{55}H_{45}As_3Cl_2OOs$: C, 54.69; H, 3.76%. Found: C, 54.95; H, 3.78%.

Di-μ-chlorobis[chlorocarbonylbis(triphenylarsine)ruthenium(II)]/1:1 dichloromethane

Into anhydrous toluene (50 ml) was placed dichlorocarbonyltris(triphenylarsine)ruthenium (0.56 g, 0.5 mmol). The solution was brought to the boil and allowed to reflux for one hour during which time the colour changed from yellow to red-orange. After removal of the solvent, the residue was dissolved in a minimum of dichloromethane and methanol was added to induce precipitation. The solid was collected and washed with methanol and n-hexane to yield the required product as an orange powder, 0.37 g (91%). M. pt. 131 °C. This low melting point is indicative of occluded solvent. Infrared, ν(CO) 1955 cm^{-1} (strong, broad). *Anal.* Calcd. for $C_{75}H_{62}As_4Cl_6O_2Ru_2$: C, 52.68; H, 3.66; Cl, 12.44%. Found: C, 52.42; H, 3.63; Cl, 11.93%.

Di-μ-chlorobis[chlorocarbonylbis(triphenylarsine)osmium(II)]

Into anhydrous toluene (50 ml) was placed dichlorocarbonyltris(triphenylarsine)osmium (0.6 g). The solution was brought to the boil and allowed to reflux for two hours during which time the colour changed from orange to yellow. After cooling the precipitate was collected and washed with methanol and n-hexane to yield the required product as a yellow powder, 0.43 g (96%). M. pt. 248 °C. Infrared, ν(CO) complex band 1960(sh), 1950(vs), 1938(m), 1921(w) cm^{-1}. *Anal.* Calcd. for $C_{74}H_{60}As_4Cl_4O_2Os_2$: C, 49.27; H, 3.32, Cl, 7.86%. Found: C, 49.35; H, 3.37; Cl, 8.65%.

Carbonylchlorohydridotris(triphenylarsine)ruthenium(II)

Solutions of hydrated ruthenium trichloride (0.27 g, 1 mmol) in 2-methoxyethanol (20 ml), aqueous formaldehyde (15 ml, 40% solution) and triethylamine (3 ml) in 2-methoxyethanol (20 ml) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylarsine (2.03 g, 6.63 mmol) in 2-methoxyethanol (75 ml). The mixture was heated under reflux for one hour during which time the colour changed to dark brown and an off-white precipitate separated. The mixture was cooled to room temperature and the solid was collected and washed as in the general experimental procedure to afford the required product as off-white microcrystals, 0.57 g (53%). M. pt. 221 °C. Infrared, ν(RuH) 1992(m), ν(CO) 1920(vs), 1900(sh) cm^{-1}. *Anal.* Calcd. for $C_{55}H_{46}As_3ClORu$: C, 60.92; H, 4.28; Cl, 3.27%. Found: C, 60.25; H, 4.19; Cl, 3.96%.

Carbonylchlorohydridotris(triphenylarsine)osmium(II)

Solutions of sodium hexachloroosmate hexahydrate (0.85 g, 1.52 mmol) in 2-methoxyethanol (20 ml), aqueous formaldehyde (15 ml, 40% solution) and triethylamine (3 ml) in 2-methoxyethanol (20 ml) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylarsine (5.52 g, 18 mmol) in 2-methoxyethanol (75 ml). The mixture was heated under reflux for one hour during which time the colour changed to dark brown and an off-white precipitate separated. The mixture was cooled to room temperature and the solid was collected and washed as in the general experimental procedure to afford the required product as off-white microcrystals, 1.05 g (58%). M. pt. 260 °C. Infrared, ν(OsH) 2080(m), ν(CO) 1900(vs), 1885(s) cm^{-1}. *Anal.* Calcd. for $C_{55}H_{46}As_3ClOOs$: C, 56.29; H, 3.96; Cl, 3.02%. Found: C, 55.85; H, 3.95; Cl, 2.57%.

Dihydridocarbonyltris(triphenylarsine)ruthenium(II)

Into anhydrous ethanol (50 ml) were placed dichlorocarbonyltris(triphenylarsine)ruthenium (0.52

g) and sodium borohydride (1.0 g). The mixture was brought to boiling and allowed to stir and reflux for 1.5 hours. After cooling, the tan slurry was filtered leaving a white solid which was washed as in the general experimental procedure to afford the required product as a white powder, 0.30 g (61%). M. pt. 172 °C. Infrared, ν(CO) 1930(s), ν(RuH) 1900(m) cm^{-1}. High field ^1H NMR spectrum τ 17.04 (doublet), τ 20.67 (doublet), ^2J (HH') 6.5 Hz. *Anal.* Calcd. for $C_{55}H_{47}As_3ORu$: C, 62.92; H, 4.52%. Found: C, 62.56; H, 4.52%.

Dihydridocarbonyltris(triphenylarsine)osmium(II)

Into anhydrous ethanol (50 ml) were placed dichlorocarbonyltris(triphenylarsine)osmium (0.51 g) and sodium borohydride (1.0 g). The mixture was brought to the boil and allowed to stir and reflux for 1.5 hours. After cooling to room temperature, the dark brown slurry was filtered leaving a white solid which was washed as in the general experimental procedure to afford the required product as a white powder, 0.34 g (70%). M. pt. 224 °C. Infrared, ν(CO) 1940(s), ν(OsH) 2038(w), 1910(s) cm^{-1}. High field ^1H NMR spectrum τ 18.10 (doublet), τ 21.78 (doublet), ^2J (HH') 5 Hz. *Anal.* Calcd. for $C_{55}H_{47}As_3OOs$: C, 57.99; H, 4.15%. Found: C, 57.62; H, 4.17%.

Dichlorodicarbonylbis(triphenylarsine)ruthenium(II)

Into anhydrous benzene (50 ml) was placed dichlorocarbonyltris(triphenylarsine)ruthenium (0.56 g, 0.5 mmol). The solution was brought to the boil and allowed to reflux for one hour during which time carbon monoxide was continuously bubbled through the solution and the colour changed from pale yellow to nearly colourless. After removal of the solvent, the residue was dissolved in a minimum quantity of dichloromethane and methanol was added to induce precipitation. The solid was collected and washed with methanol and hexane to yield the required product as a cream white powder 0.36 g (87%). M. pt. >300 °C. Infrared, ν(CO) 2059(s), 1999(s) cm^{-1}. *Anal.* Calcd. for $C_{38}H_{30}As_2Cl_2O_2Ru$: C, 54.30; H, 3.60%. Found: C, 53.25; H, 3.57%.

Dichlorodicarbonylbis(triphenylarsine)osmium(II)

Similarly prepared from dichlorocarbonyltris(triphenylarsine)osmium as a very pale cream powder (91%). M. pt. >300 °C. Infrared (CH_2Cl_2 solution), ν(CO) 2040(s), 1975(s) cm^{-1}. *Anal.* Calcd. for $C_{38}H_{30}As_2Cl_2O_2Os$: C, 49.09; H, 3.26%. Found: C, 48.95; H, 3.26%.

Chlorohydridodicarbonylbis(triphenylarsine)ruthenium(II)

Into anhydrous benzene (50 ml) was placed chlorohydridocarbonyltris(triphenylarsine)ruthenium (0.54 g, 0.5 mmol). The solution was brought to the boil and allowed to reflux for one hour during which time carbon monoxide was continuously bubbled through the solution and the colour changed from yellow to colourless. After removal of the solvent, the residue was dissolved in a minimum quantity of dichloromethane and methanol was added to induce precipitation. The solid was collected and washed with methanol and hexane to yield the required product as a white powder, 0.36 g (90%). M. pt. 296 °C. Infrared ν(CO) 2060(s), 2000(s) cm^{-1}. *Anal.* Calcd. for $C_{38}H_{31}As_2ClO_2Ru$: C, 56.62; H, 3.88%. Found: C, 56.56; H, 3.87%.

Chlorohydridodicarbonylbis(triphenylarsine)osmium-(II)

Similarly prepared from 0.58 g (0.5 mmol) chlorohydridocarbonyltris(triphenylarsine)osmium(II); the required complex was a white powder, 0.40 g (91%). M. pt. 246 °C. Infrared, 2020(s), 1958(s), 1900(w) cm^{-1}. *Anal.* Calcd. for $C_{38}H_{31}As_2ClO_2Os$: C, 50.98; H, 3.50%. Found: C, 50.88; H, 3.46%.

Attempted Preparation of Dihydridotetrakis(triphenylarsine)ruthenium(II)

Solutions of ruthenium trichloride trihydrate (0.13 g, 0.5 mmol) in ethanol (10 ml) and sodium borohydride (0.13 g) in ethanol (10 ml) were added rapidly and successively to a boiling solution of triphenylarsine (0.92 g, 3 mmol) in ethanol (40 ml). The dark brown mixture was heated under reflux for 5 min then cooled and filtered. The filter cake was washed successively with ethanol, water and ethanol then dried *in vacuo* to yield a fine dark chocolate brown powder (0.40 g). M. pt. 200–210 °C with charring. *Anal.* Found: C, 59.69; H, 4.63%.

Tetrahydridotris(triphenylarsine)osmium(IV)

Warm solutions of sodium hexachloroosmate hexahydrate (0.57 g, 1 mmol) in ethanol (20 ml) and sodium borohydride (0.25 g) in ethanol (20 ml) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylarsine (1.88 g, 6.14 mmol) in ethanol (80 ml). *Vigorous frothing occurs.* The pink reaction mixture was heated under reflux for 30 min during which time a grey solid separates. After cooling, the precipitate was collected and washed as in the general experimental procedure to yield the required product as grey microcrystals, 0.63 g (57%). M. pt. 212 °C. Infrared, ν(OsH) 2080(s), 2060(w), 2000(m), 1850(s) cm^{-1}. *Anal.* Calcd. for $C_{54}H_{49}As_3Os$: C, 58.22; H, 4.45%. Found: C, 57.70; H, 4.39%.

Attempted preparation of hydridotetrakis(triphenylarsine)rhodium

Solutions of rhodium trichloride trihydrate (0.26 g, 1.0 mmol) in ethanol (20 ml) and sodium boro-

hydride (0.26 g) in ethanol (10 ml) were added rapidly and successively to a boiling solution of triphenylarsine (3.0 g, 10 mmol) in ethanol (80 ml). After 3 min the warm mixture was filtered and the residue washed successively with methanol, water methanol and n-hexane then dried *in vacuo* to afford a fine mustard yellow powder (0.86 g). M. pt. 185–187 °C after charring at 180 °C. Infrared, ν(RhH) 2100(w) cm^{-1}. High field ^1H NMR spectrum τ 20.69(br,s). *Anal.* Calcd. for $C_{72}H_{61}As_4Rh$, C, 65.07; H, 4.63%. Found: C, 66.42; H, 4.92%.

Fac-trihydridotris(triphenylarsine)iridium(III)

Warm solution of sodium hexachloroiridate (0.85 g, 1.5 mmol) in ethanol (20 ml) and sodium borohydride (0.35 g) in ethanol (30 ml) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylarsine (3.75 g, 12 mmol) in ethanol (120 ml). *There is much frothing and evolution of hydrogen on addition of the sodium borohydride solution.* The mixture was heated under reflux for 30 min during which time it became dirty-yellow in colour with a small amount of grey precipitate. After cooling to room temperature, the precipitate was collected and washed as in the general experimental procedure to afford the required product as grey microcrystals, 1.05 g (62%). M. pt. 224 °C. Infrared, ν(IrH) 2090(s) cm^{-1}. High field ^1H NMR spectrum τ 23.52 (s). *Anal.* Calcd. for $C_{54}H_{48}As_3Ir$: C, 58.20; H, 4.35%. Found: C, 57.75; H, 4.39%.

Chlorodihydridotris(triphenylarsine)iridium(III)

Sodium chloroiridate (0.19 g, 0.33 mmol) in 2-methoxyethanol (10 ml) and triethylamine (0.5 ml) were added rapidly and successively to a boiling solution of triphenylarsine (0.92 g, 3 mmol) in 2-methoxyethanol (20 ml). The resultant pale yellow solution was heated under reflux for 5 min, cooled and then evaporated to small volume on a rotary evaporator. Addition of methanol (10 ml) led to slow deposition of a white precipitate which was purified as described in the general experimental procedure to afford the required product as white microcrystals, (0.27 g, 71%). M. pt. 219–221 °C. Infrared, ν(IrH) 2150(s) and 2130(s) cm^{-1}. High field ^1H NMR spectrum (C_6D_6) τ 23.87(d) and τ 32.74(d) $^2J(HH') = 6$ Hz. *Anal.* Calcd. for $C_{54}H_{47}As_3ClIr$: C, 56.48; H, 4.13%. Found: C, 56.90; H, 4.17%.

Dichlorohydridotris(triphenylarsine)iridium(III)

This was similarly prepared using N-methyl-N-nitrosotoluene-P-sulphonamide (0.2 g in 2-methoxyethanol, 5 ml) in place of triethylamine and heating the resultant yellow solution for *ca.* 20 min. Isolation as described above followed by recrystallisation from dichloromethane–methanol gave the required product as pale yellow microcrystals. (0.31 g, 79%). M. pt. 240–245 °C. Infrared, ν(IrH) 2160(m) cm^{-1}. High field ^1H NMR spectrum τ 31.37 (s). *Anal.* Calcd. for $C_{54}H_{46}As_3Cl_2Ir$: C, 54.83; H, 3.92%. Found: C, 55.21; H, 4.15%.

Trichlorotris(triphenylarsine)iridium(III)

This was similarly prepared using concentrated hydrochloric acid (0.25 ml) in place of triethylamine and on cooling the reaction solution deposited as bright yellow-orange crystals, (0.35 g, 86%). M. pt. 251–252 °C. *Anal.* Calcd. for $C_{54}H_{45}As_3Cl_3Ir$: C, 53.29; H, 3.73%. Found: C, 53.69; H, 3.9%.

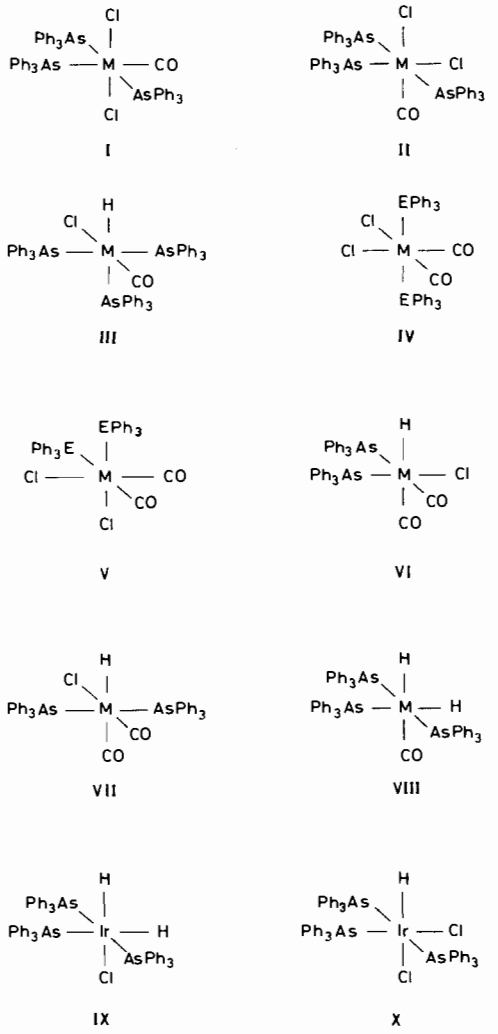
Results and Discussion

Complexes $[MCl_2(CO)(AsPh_3)_3]$ (M = Ru or Os)

Addition of the appropriate metal chloride or chloro complex and 40% aqueous formaldehyde to a solution of triphenylarsine in boiling 2-methoxyethanol affords the dichlorides $[MCl_2(CO)(AsPh_3)_3]$ as pale yellow (M = Ru) or orange (M = Os) air-stable crystals. Apparently the basicity of the triphenylarsine is insufficient to promote the base/alcohol conversion of a chloride ligand to hydride under the conditions employed in these syntheses. Stephenson *et al.* [8] have described a synthesis of $[RuCl_2(CO)(AsPh_3)_3]$ based on the addition of triphenylarsine to the 'red solution' obtained by carbonylation of ethanolic ruthenium trichloride. However, the infrared spectrum reported for their product [ν(CO) 2010(w) 1961 cm^{-1}] differs from that of our own [ν(CO) 1948, 1912 cm^{-1}], and it appears probable that we are dealing with different isomers. The osmium complex $[OsCl_2(CO)(AsPh_3)_3]$ does not appear to have previously been described. Complexes of the stoichiometry $[MCl_2(CO)L_3]$ (M = Ru or Os, L = P or As donor ligand) commonly exist in one or both of the isomeric forms represented in (I) and (II) (L = $AsPh_3$). Comparisons with similar data previously recorded for related complexes suggest that the relatively low values of ν(CO) found for our complexes $[MCl_2(CO)(AsPh_3)_3]$ are indicative of stereochemistry (II) with carbonyl *trans* to chloride. Thus Stephenson's complex, $[RuCl_2(CO)(AsPh_3)_3]$ [8] which displays a significantly higher value of ν(CO) presumably possesses stereochemistry (I). In order to authenticate our products they have been carbonylated and reduced to yield the dicarbonyls $[MCl_2(CO)_2(AsPh_3)_2]$ and the dihydrides $[MH_2(CO)(AsPh_3)_3]$ respectively (*vide infra*).

Complexes $[MHCl(CO)(AsPh_3)_3]$ (M = Ru or Os)

If the syntheses discussed above are repeated with addition of triethylamine to compensate for the low basicity of triphenylarsine relative to triphenylphosphine, abstraction of hydride ligands



from the alcohol solvent occurs and the hydridochloro complexes $[MHCl(CO)(AsPh_3)_3]$ separate in good yield. These complexes have previously been synthesised by a similar method involving use of a higher boiling point alcohol rather than the addition of a nitrogen base to achieve the desired hydride abstraction [10]. However, only the osmium complex has been fully characterised [11]. These complexes have previously been assigned stereochemistry (III) by analogy with the corresponding triphenylphosphine complex $[OsHBr(CO)(PPh_3)_3]$ which has been shown by X-ray diffraction methods to possess a similar structure [12]. Stereochemistry (III) has also been assigned to a range of related phosphine and arsine complexes $[RuHCl(CO)L_3]$ (L = P or As donor ligand) [9]. Our observation that the complexes $[MHCl(CO)(AsPh_3)_3]$ cannot be converted to the corresponding dihydrides $[MH_2(CO)(AsPh_3)_3]$ by borohydride reduction is consistent with the presence of chloride *trans* to the weak *trans* effect CO ligand and therefore also supports stereochemistry (III).

Complexes $[MCl_2(CO)(AsPh_3)_2]_2$ (M = Ru or Os)

The poor coordinating power of triphenylarsine relative to the corresponding phosphine is illustrated by the ease with which the complexes $[MCl_2(CO)(AsPh_3)_3]$ lose a triphenylarsine ligand in boiling toluene to afford yellow (M = Os) or orange (M = Ru) binuclear chloro-bridged species of stoichiometry $[\{(MCl_2(CO)(AsPh_3)_2\}_2]$. These products are too insoluble for solution studies, in particular conductivity measurements and precipitation reactions, we cannot therefore exclude an alternative ionic formulation $[(Ph_3As)_2(CO)MCl_3M(CO)(AsPh_3)_2]Cl$ of the type commonly found in ruthenium(II) and osmium(II) phosphine chemistry [13]. Formulation as five coordinate monomers is also possible but this configuration is considered highly unlikely. The complexity of the infrared [ν(CO)] spectra may reflect the presence of a mixture of isomeric products.

Complexes $[MCl_2(CO)_2(AsPh_3)_2]$ (M = Ru or Os)

Carbonylation of the monocarbonyls $[MCl_2(CO)(AsPh_3)_3]$ under mild conditions affords the corresponding dicarbonyls $[MCl_2(CO)_2(AsPh_3)_2]$ in high yield as air-stable microcrystalline solids. These complexes have previously been prepared by addition of triphenylarsine to the appropriate metal carbonyl halides [14, 15] and, in the case of the ruthenium complex, by treatment of $[Ru_3(CO)_{12}]$ with triphenylarsine in the presence of chloroform [16]. The infrared spectra of our products, which agree well with those previously reported, show two strong ν(CO) vibrations consistent with the presence of a mutually *cis* pair of carbonyl ligands in each complex. Solid state splittings observed for each ν(CO) band in the spectrum of the osmium complex (nujol) are absent from the solution (CH_2Cl_2) spectrum. On the basis of infrared spectra and dipole moment measurements the ruthenium [14] and osmium [15] complexes have been assigned structures (IV) and (V) respectively. However, other authors [17] claim that the related osmium triphenylphosphine complex $[OsCl_2(CO)_2(PPh_3)_2]$, which was also assigned stereochemistry (V) on similar evidence, really possesses stereochemistry (IV). A sample of $[OsCl_2(CO)_2(PPh_3)_2]$ identical with the material discussed above was prepared in our laboratory by treatment of $[OsH_2(CO)_2(PPh_3)_2]$ with carbon tetrachloride [18], and was shown by ^{31}P NMR (δP – 13.24, singlet) to possess struture (IV) rather than (V). We therefore conclude that all the dicarbonyl complexes of general formula $[MCl_2(CO)_2(EPh_3)_2]$ discussed above probably possess stereochemistry (IV) but note that our data do not entirely exclude a structure with *trans*

chloride and *cis* carbonyl ligands. Our observation that the dicarbonyl complexes are not converted to the corresponding dihydrides $[MH_2(CO)_2(AsPh_3)_2]$ by treatment with sodium borohydride in boiling ethanol is consistent with the presence of the weakly *trans*-labilising carbonyl groups *trans* to the chloride ligands, and therefore supports the assignment of stereochemistry (IV).

Complexes $[MHCl(CO)_2(AsPh_3)_2]$ (M = Ru or Os)

These white air-stable crystalline complexes are readily prepared in good yield by carbonylation of the corresponding monocarbonyls $[MHCl(CO)(AsPh_3)_3]$ and, unlike their precursors, are sufficiently soluble for proton NMR spectroscopy. Each complex displays a high field singlet [τ_{RuH} 15.6; τ_{OsH} [13.7] with chemical shift values indicative of hydride *trans* to carbonyl rather than triphenylarsine and therefore consistent with structures (VI) and (VII). However, since the complexes $[MHCl(CO)_2(AsPh_3)_2]$ are not reduced to the corresponding dihydrides $[MH_2(CO)_2(AsPh_3)_2]$ by borohydride in ethanol, it appears probable that they contain chloride *trans* to a weakly *trans*-labilising carbonyl ligand and therefore possess stereochemistry (VII). This geometry has also been established for the related triphenylphosphine complex $[RuHCl(CO)_2(PPh_3)_2]$ [19].

Complexes $[MH_2(CO)(AsPh_3)_3]$ (M = Ru or Os)

These white air-stable crystalline complexes are readily obtained in excellent yield by borohydride reduction of the corresponding dichlorides $[MCl_2(CO)(AsPh_3)_3]$. The high field proton NMR spectrum of each complex consists of a pair of doublets [$^2J(HH')$ = *ca.* 5 Hz] indicative of stereochemistry (VIII) – the same as that previously reported for the corresponding phosphine complexes $[MH_2(CO)(PPh_3)_3]$ [3]. Attempts to prepare the dicarbonyls $[MH_2(CO)_2(AsPh_3)_2]$ by carbonylation of the monocarbonyls $[MH_2(CO)(AsPh_3)_3]$ under mild conditions (boiling benzene) were unsuccessful, only unchanged starting material was recovered.

Attempted Preparation of the Complex $[RuH_2(AsPh_3)_4]$

The borohydride reduction technique previously used to prepare $[RuH_2(PPh_3)_4]$ [2] does not provide a route to the corresponding arsine complex. Instead reduction of ruthenium trichloride by ethanolic sodium borohydride in the presence of triphenylarsine consistently affords, in very good yield, a fine dark chocolate brown powder which has analytical data compatible with the formulation '$Ru(AsPh_3)_2$'. The infrared spectrum of this product is essentially identical with that of triphenylarsine, in particular it shows no absorptions attributable to hydride or carbonyl ligands. The complex, which is air-stable in the solid state and dissolved in chlorinated hydrocarbons to afford very dark brown solutions, has not been identified.

Complex $[OsH_4(AsPh_3)_3]$

This complex was first mentioned in our earlier report [20] on the corresponding triphenylphosphine complex $[OsH_4(PPh_3)_3]$ but has not previously been fully described. A related arsine complex $[OsH_4(AsMe_2Ph)_3]$ has also been reported [21]. The proton NMR spectrum of $[OsH_4(AsPh_3)_3]$ displays a high field resonance [τ_{OsH} 21.7(s)] consistent with a structure in which all the hydride ligands are rendered magnetically equivalent by a rapid intramolecular rearrangement.

Attempted Preparation of the Complex $[RhH(AsPh_3)_4]$

Reduction of rhodium trichloride with sodium borohydride in the presence of triphenylarsine affords, in excellent yield, a mustard yellow powder similar in appearance to the well-established triphenylphosphine complex $[RhH(PPh_3)_4]$ [2]. The new product has an infrared spectrum which contains a weak band (2010 cm^{-1}) attributable to ν(RhH) but is otherwise identical with that of triphenylarsine. The high field NMR spectrum of the new product displays a broad resonance at τ 20.81. However, the low intensity of this signal suggests that the hydride concentration is not more than *ca.* 50% of the theoretical value, and that the product contains substantial amounts of a non-hydride species having analytical and infrared spectroscopic data similar to those of $[RhH(AsPh_3)_4]$. A likely contaminant is the *ortho* metallated complex $[Rh(C_6H_4AsPh_2)(AsPh_3)_3]$; however, since the infrared bands expected for *ortho* metallated phenyl rings occur in regions of the spectrum masked by the absorptions of triphenylarsine ligands the presence of this species cannot be confirmed.

Complexes $[IrH_nCl_{3-n}(AsPh_3)_3]$ (n = 0–3)

These complexes are readily obtained in good yield by addition of sodium chloroiridate to boiling solutions of triphenylarsine in 2-methoxyethanol in the presence of sodium borohydride (n = 3), triethylamine (n = 2), N-methyl-N-nitrosotoluene-*p*-sulphonamide (n = 1) or hydrochloric acid (n = 0). N-methyl-N-nitroso-toluene-*p*-sulphonamide is widely used as a reagent to replace hydride ligands by nitrosyl groups. However, in the present reaction it appears to function as a mild base in the formation of $[IrHCl_2(AsPh_3)_3]$ but fails to react further with this product.

Both *mer* and *fac* isomers of $[IrH_3(AsPh_3)_3]$ have previously been prepared by a multistage synthesis involving borohydride reduction of $[IrHBr_2(AsPh_3)_3]$ [22]. The single step synthesis discussed

above yields a pure product which, on the evidence of its high field proton NMR spectrum [τ_{IrH} 23.52(s)] can be assigned *fac* stereochemistry. The dihydride [$IrH_2Cl(AsPh_3)_3$] has previously been prepared [6] by addition of dihydrogen to [$IrCl(AsPh_3)_3$]; However, in the absence of a high field proton NMR spectrum its stereochemistry was not determined. Our sample can be assigned stereochemistry (IX) on the basis of a high field proton NMR pattern comprising a pair of doublets [$^2J(HH') = 6$ Hz]. The monohydride [$IrHCl_2(AsPh_3)_3$] has also been previously reported [6, 23] but again no stereochemical assignment was given. On the basis of the high tau value (τ 31.37) recorded for the hydride ligand in this complex we conclude that it is *trans* to chloride rather than triphenylarsine and therefore assign stereochemistry (X) similar to that postulated for the corresponding triphenylphosphine complex [6]. Although the complex [$IrCl_3(AsPh_3)_3$] does not appear to have previously been reported, related tertiary arsine complexes [$IrCl_3(AsR_3)_3$] are known and adopt *mer* or *fac* stereochemistry [24].

Stereochemical analysis of [$IrCl_3(AsPh_3)_3$] was achieved by examining the aromatic region of the ^1H NMR spectrum of the complex in C_6D_6. This clearly indicated the presence of a *trans* pair of triphenylarsine ligands [25] and thus established a *mer* configuration for the complex.

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