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Triphenyl-phosphine and -arsine analogues which facilitate the electrospray mass spectrometric analysis of neutral metal complexes

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The six triarylphosphines $PPh_n(C_6H_4OMe\text{-}p)_{3-n}$ and $PPh_n(C_6H_4NMe_2\text{-}p)_{3-n}$ ($n = 0$–3) and the arsine $As(C_6H_4OMe\text{-}p)_3$ (L) have been synthesized and examined for their use in the electrospray mass spectrometric (ESMS) study of metal complexes. This has been tested with selected examples of the complexes $[Mo(CO)_4L_2]$, $[Fe(CO)_3L_2]$, $[Fe(CO)_4L]$, $[Ru_3(CO)_9L_3]$, *cis*-$[PtCl_2L_2]$, $[PdCl_2L_2]$ and [AuCl(L)]. All of the metal carbonyl complexes of these ligands gave $[M + H]^+$ ions in their spectra, while in contrast the analogous PPh_3 complexes do not, suggesting that these electrospray-friendly ligands should be useful for the characterisation of a wide range of complexes by ESMS. The incorporation of the ligands into metal halide complexes however does not allow the observation of $[M + H]^+$ ions, with ions formed by the previously reported halide-loss mechanism being the only ones observed.

Introduction

Electrospray (ES) is a relatively recent mass spectrometric ionisation technique, which is proving to be invaluable in the armoury of the co-ordination and organometallic chemist.[1] In general, the only proviso for the successful detection of ions using this method is solubility in an appropriate solvent, together with a means by which the parent molecule, if uncharged, can become ionised. Often, this is by attachment of a proton (or another cation such as NH_4^+ or Na^+) to some basic site (typically an oxygen or nitrogen atom with a lone pair). In some cases, compounds do not readily ionise using these "standard" ESMS conditions, in which case it is necessary to perform some chemical derivatisation step in order to generate charged species. This is well illustrated by the addition of either alkoxide[2] or azide[3] ions to neutral transition metal carbonyl complexes; the resulting ions, formed by nucleophilic attack of the anion at a co-ordinated CO, are readily analysed by ESMS. Other pathways by which ionisation of transition metal complexes can occur are electrochemical oxidation in the metal capillary of the instrument,[4] and by loss of an anionic ligand, typically a halide.[5,6]

Since the protonation pathway for ionisation is potentially the most general, and is gentle in nature, we wished to extend its usefulness by the development of ligands which contain suitable basic substituents. In this paper we describe our studies on tertiary phosphines and arsines. Tertiary phosphines are ubiquitous in organometallic and co-ordination chemistry, and their complexes find numerous applications, ranging from catalysis[7] to medicine.[8] Triphenylphosphine is perhaps the archetypal phosphine ligand, yet its presence in a complex offers no pathway for ionisation, which must instead rely on ionisation from other parts of the complex, by protonation, oxidation, halide loss, *etc*. We reasoned that the use of protonatable methoxy or dimethylamino substituted triphenylphosphines, -arsines, and -stibines would facilitate the protonation ionisation pathway. The derivatisation of molecules with readily ionisable substituents is not a new concept, for example the incorporation of ferrocene substituents for electrochemical ionisation,[9] the use of 4-aminobenzoic acid 2-(diethylamino)-ethyl ester for the derivatisation of oligosaccharides and analysis by protonation[10] and the use of a protonatable pyridyl bromide in the detection of intermediates (by ESMS) in the Suzuki coupling of phenylboronic acids and aryl halides.[11] However, the routine use of electrospray-friendly ligands to facilitate mass spectrometric analysis is rare in inorganic chemistry.

In comparison with the chemistry of phosphines, that of related arsines (and especially stibines) is far less well developed, and in part this is likely to be due to the lack of readily accessible NMR-active nuclei for As and Sb when compared to the ^{31}P nucleus.[12] A new method of monitoring reactions involving arsine and stibine ligands should encourage further development of their chemistry.

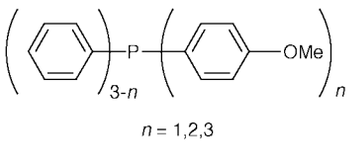
Results and discussion

Ligand choice and synthesis

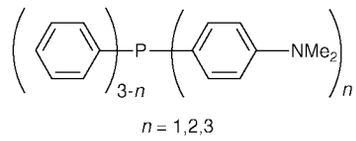
The "electrospray-friendly" ligands chosen for this study are derived from the very widely employed PPh_3 and $AsPh_3$. Functionalised analogues, containing OMe or NMe_2 groups in *para* positions on one to three phenyl rings, were chosen, because of their overall similarity to the parent ligand. Structures of the ligands are shown below.

A key aim of this project was to use ligands which are similar in most respects to the parent PPh_3 or $AsPh_3$ ligands, so that the fundamental chemistry is essentially unchanged. Accordingly, the *para* isomers were chosen (instead of the *ortho* or *meta*) so that the steric properties of the ligands are very similar. Thus, the steric properties of PPh_3 and $P(C_6H_4OMe\text{-}p)_3$ are identical,[13] both having cone angles of 145° while their electronic properties are reasonably similar, as usually expressed by the pK_a values of the protonated phosphines of 2.73 and 4.59 respectively.[14] Some related triphenylphosphine-derived ligands, containing OMe and/or SMe groups in *ortho* and *para* positions, have recently been reported, though no detailed MS studies were carried out.[15]

The $P(C_6H_4OMe\text{-}p)_3$ and $P(C_6H_4NMe_2\text{-}p)_3$ ligands, and their metal complexes, are generally expected to be more soluble in organic solvents than their PPh_3 analogues, so if a very close similarity is desired, then $PPh_2(C_6H_4OMe\text{-}p)$ and $PPh_2(C_6H_4NMe_2\text{-}p)$ are more appropriate. On the other hand, it was anticipated that the ligands (and complexes) bearing the



n = 1,2,3



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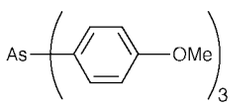

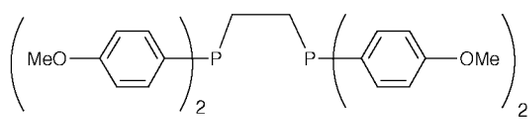

greatest number of OMe or NMe_2 substituents might provide the best ES spectra. A comparison of the ligands in terms of their ionisation efficiencies and electronic similarities was carried out, and results are discussed later in this paper.

The ligands are all known from previous studies and were readily prepared by reaction of the appropriate Grignard reagent with PCl_3, $PhPCl_2$, Ph_2PCl or $AsCl_3$ as appropriate. All are air-stable crystalline solids, similar to PPh_3 and $AsPh_3$. While the ligands can easily be prepared from inexpensive starting materials, some are also commercially available.

Synthesis and characterisation of metal complexes

A wide range of metal complexes of the methoxy- and amino-substituted phosphines has been prepared following procedures previously published for the PPh_3 and $AsPh_3$ analogues. These are listed in Table 1. The examples were chosen to cover two main types of complex. Neutral metal phosphine(arsine) carbonyl complexes of molybdenum, iron and ruthenium were examined, since the PPh_3 analogues do not give ES spectra. The second group involved metal phosphine halide complexes of platinum, palladium and gold, chosen to evaluate the tendency (if any) of these complexes to undergo ionisation by protonation compared to ionisation by halide loss, which is the ionisation pathway previously observed for other complexes of this type.[5,6] Selected PPh_3 and $AsPh_3$ complexes were also synthesized for comparative purposes. Complexes **2c**, **4f**, **5b** and **6f** have been synthesized previously (see Experimental section), but the others appear to be new. Characterisation data for the new complexes are given in Table 1.

In order to confirm the close similarity of the functionalised ligands compared to their PPh_3 or $AsPh_3$ analogues a ^{31}P NMR and IR spectroscopic survey has been carried out. Generally, increasing numbers of OMe or NMe_2 groups in the ligand cause a slight shift of CO stretching bands to lower wavenumbers, due to increased back donation with a slightly more electron-rich phosphine. However, the values are overall similar to those of the PPh_3 analogues. This is well illustrated by the series of $[Mo(CO)_4L_2]$ complexes, where there is a *ca.* 10 cm^{-1} shift in CO stretching frequency going from $[Mo(CO)_4(PPh_3)_2]$ to $[Mo(CO)_4\{P(C_6H_4NMe_2\text{-}p)_3\}_2]$. Similar trends are observed for the iron carbonyl complexes and the stronger bands of the ruthenium carbonyl complexes. These observations are paralleled by the ^{31}P NMR chemical shifts, where shielding of the ^{31}P nucleus occurs on incorporation of OMe or NMe_2 groups. Thus, as shown in Table 1, there is a small stepwise decrease in the $\delta(^{31}P)$ value from $[Mo(CO)_4(PPh_3)_2]$ (38.9), to $[Mo(CO)_4\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$ (37.1) to $[Mo(CO)_4\{PPh(C_6H_4OMe\text{-}p)\}_2]$ (35.5) to $[Mo(CO)_4\{P(C_6H_4OMe\text{-}p)_3\}_2]$ (34.0). Very approximately, the presence of two NMe_2 groups (in **1d**) has around the same effect on the ^{31}P NMR shift as four OMe groups (in **1b**). Similar trends in $\delta(^{31}P)$ were observed for the other series of complexes, with NMe_2 substituted complexes having lower values than the analogous complexes with OMe substituents.

Electrospray mass spectrometry

(a) Metal carbonyl complexes. Table 2 lists the ions observed in the ES spectra of the metal carbonyl complexes **1**–**3** and **7**–**8**. The neutral complexes $[Mo(CO)_4(PPh_3)_2]$ **1**, $[Fe(CO)_3(PPh_3)_2]$ **2**, $[Ru_3(CO)_9(PPh_3)_3]$ **3**, $[Mo(CO)_4(AsPh_3)_2]$ **7** and $[Fe(CO)_3(AsPh_3)_2]$ **8** did not give ions in their ES spectra, as expected with the absence of basic sites for protonation. In contrast, all of the neutral metal carbonyl complexes which contain the amine- or methoxy-modified ligands ionise readily, and give good ES spectra with strong $[M + H]^+$ ions. In some cases, $[M + NH_4]^+$ ions were also observed, but their intensities were generally low. The crude product from the attempted synthesis of $[Fe(CO)_3\{As(C_6H_4OMe\text{-}p)_3\}_2]$ was found by ESMS to be a mixture of this complex together with the monosubstituted complex $[Fe(CO)_4\{As(C_6H_4OMe\text{-}p)_3\}]$, demonstrating the usefulness of the technique in determining product formation in such ligand substitution reactions. However, upon recrystallisation, only the monosubstituted complex was obtained, and analytical data are reported for this complex only.

At low skimmer cone voltages, between 5 and 20 V, there is no fragmentation of the parent ions, so the parent $[M + H]^+$ ions can readily be assigned by comparison of experimental and calculated isotope distribution patterns. Such lack of fragmentation is typical for the ES process when low cone voltages are used. On increasing the cone voltage, carbonyl ligands are lost sequentially, as illustrated in Fig. 1 for $[Ru_3(CO)_9\{PPh_2(C_6H_4OMe\text{-}p)\}_3]$ **3a**. Similar loss of carbonyl ligands has been observed previously, *e.g.* in studies of neutral metal carbonyl complexes investigated using alkoxide[2] or azide[3] ionisation.

Having established the generality of the use of the derivatised phosphines, it was of interest to carry out a comparison of the ionisation efficiencies of the different ligands, to compare the effect of an oxygen with a more basic nitrogen, and of one substituent per ligand *versus* two or three. An equimolar mixture of the complexes $[Mo(CO)_4\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$ **1a**, $[Mo(CO)_4\{PPh(C_6H_4OMe\text{-}p)_2\}_2]$ **1b** and $[Mo(CO)_4\{P(C_6H_4OMe\text{-}p)_3\}_2]$ **1c** was prepared in methanol solution and analysed by ESMS. The relative intensities of the $[M + H]^+$ ions increase (24 : 51 : 100) directly in proportion to the increasing number of MeO groups in the complex from 2 to 4 to 6, as shown in Fig. 2. In a separate experiment to compare the ionisation efficiencies of OMe substituted complexes *versus* NMe_2 substituted complexes, a 1 : 1 mixture of **1b** and $[Mo(CO)_4\{PPh(C_6H_4NMe_2\text{-}p)_2\}_2]$ **1e** was analysed. In this case, the NMe_2-substituted complex showed a much greater ionisation efficiency, with the methoxy analogue appearing at only 20% relative intensity to the base peak of $[Mo(CO)_4\{PPh(C_6H_4NMe_2\text{-}p)_2\}_2 + H]^+$.

The ESMS analysis using the substituted ligands appears to be very sensitive; using a series of dilutions, the complex $[Ru_3(CO)_9\{PPh_2(C_6H_4NMe_2\text{-}p)_3\}_3]$ **3d** was able to be detected down to concentrations of *ca.* 7×10^{-8} mol L^{-1}, without any special attempts to optimise signal intensity. For routine characterisation, however, we typically use more concentrated solutions (*ca.* 1 mg mL^{-1}).

For these complexes where competing ionisation is not possible, even one OMe or NMe_2 group is sufficient to provide ions with a good signal to noise ratio. In protic solvents such as

Table 1 Characterisation data for the complexes[a]

Complex	Colour	mp/°C	Elemental analysis (%)[b] C	H	N	^{31}P NMR[c] (δ)	IR CO $\tilde{\nu}_{max}$/cm^{-1}
1 $[Mo(CO)_4(PPh_3)_2]$	Bright yellow					38.9	2023s, 1927 (sh), 1908s, 1897 (sh)[d]
1a $[Mo(CO)_4\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$	Bright yellow	149–150	63.36 (63.64)	4.25 (4.33)	0.00 (0.00)	37.1	2021s, 1919 (sh), 1906s, 1879 (sh)[d]
1b $[Mo(CO)_4\{PPh(C_6H_4OMe\text{-}p)_2\}_2]$	Bright yellow	144–145	61.66 (61.98)	4.46 (4.50)	0.00 (0.00)	35.5	2020s, 1918 (sh), 1905s, 1876 (sh)[d]
1c $[Mo(CO)_4\{P(C_6H_4OMe\text{-}p)_3\}_2]$	Bright yellow	142–143	60.08 (60.53)	4.66 (4.65)	0.00 (0.00)	34.0	2018s, 1917 (sh), 1904s, 1874 (sh)[d]
1d $[Mo(CO)_4\{PPh_2(C_6H_4NMe_2\text{-}p)\}_2]$	Bright yellow	142–148	64.37 (64.56)	4.75 (4.89)	3.37 (3.42)	36.0	2019s, 1920 (sh), 1903s, 1875 (sh)[d]
1e $[Mo(CO)_4\{PPh(C_6H_4NMe_2\text{-}p)_2\}_2]$	Bright yellow	166–167	62.92 (63.72)	5.79 (5.53)	6.20 (6.20)	33.3	2016s, 1913 (sh), 1899s, 1872 (sh)[d]
1f $[Mo(CO)_4\{P(C_6H_4NMe_2\text{-}p)_3\}_2]$	Bright yellow	155–160	62.93 (63.04)	6.18 (6.06)	8.59 (8.49)	30.8	2013s, 1907 (sh), 1900s, 1873 (sh)[d]
2 $[Fe(CO)_3(PPh_3)_2]$	Dark yellow					83.1	1884[d]
2a $[Fe(CO)_3\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$	Dark yellow	220–221	67.16 (67.97)	4.60 (4.74)	0.00 (0.00)	81.3	1882[d]
2b $[Fe(CO)_3\{PPh(C_6H_4OMe\text{-}p)_2\}_2]$	Dark yellow	222–223	65.08 (65.83)	4.82 (4.89)	0.00 (0.00)	79.5	1880[d]
2c $[Fe(CO)_3\{P(C_6H_4OMe\text{-}p)_3\}_2]$	Dark yellow					77.8	1874[d]
3 $[Ru_3(CO)_9(PPh_3)_3]$	Deep red					38.0	2044w, 1979 (sh), 1967s (br)[e]
3a $[Ru_3(CO)_9\{PPh_2(C_6H_4OMe\text{-}p)\}_3]$	Deep red	138–144	54.73 (55.35)	4.03 (3.06)	0.00 (0.00)	36.7	2043w, 1979 (sh), 1967s[f]
3b $[Ru_3(CO)_9\{PPh(C_6H_4OMe\text{-}p)_2\}_3]$	Deep red	134–142	53.82 (54.44)	3.89 (3.78)	0.00 (0.00)	35.8	2047w, 1978 (sh), 1967s[f]
3c $[Ru_3(CO)_9\{P(C_6H_4OMe\text{-}p)_3\}_3]$	Deep red	118–120	53.62 (53.63)	4.36 (3.95)	0.61 (0.00)	34.6	2054w, 1977 (sh), 1966s[f]
3d $[Ru_3(CO)_9\{PPh_2(C_6H_4NMe_2\text{-}p)\}_3]$	Deep red	140–142	55.65 (56.32)	3.89 (4.08)		36.0	2054w, 1977 (sh), 1965s[f]
3e $[Ru_3(CO)_9\{PPh(C_6H_4NMe_2\text{-}p)_2\}_3]$	Deep red	148–150	56.21 (56.27)	4.86 (4.69)		34.3	2055w, 1972 (sh), 1963s[f]
3f $[Ru_3(CO)_9\{P(C_6H_4NMe_2\text{-}p)_3\}_3]$	Deep red	160–165	54.71 (56.24)	5.44 (5.21)		32.7	2054w, 1970 (sh), 1959s[f]
4 *cis*-$[PtCl_2(PPh_3)_2]$	White					15.1 (3673)	
4a *cis*-$[PtCl_2\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$	White	258–259	51.52 (53.65)	4.00 (4.04)	0.00 (0.00)	13.8 (3684)	
4b *cis*-$[PtCl_2\{PPh(C_6H_4OMe\text{-}p)_2\}_2]$	White	242–243	52.29 (52.75)	4.16 (4.21)	0.00 (0.00)	12.7 (3695)	
4c *cis*-$[PtCl_2\{P(C_6H_4OMe\text{-}p)_3\}_2]$	White					11.5 (3705)	
4f *cis*-$[PtCl_2\{P(C_6H_4NMe_2\text{-}p)_3\}_2]$	White					9.7 (3758)	
5 $[PdCl_2(PPh_3)_2]$	Deep yellow					24.0	
5a $[PdCl_2\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$	Deep yellow	175–176	58.59 (59.90)	4.50 (4.51)	0.00 (0.00)	22.8	
5b $[PdCl_2\{PPh(C_6H_4OMe\text{-}p)_2\}_2]$	Deep yellow					21.6	
5c $[PdCl_2\{P(C_6H_4OMe\text{-}p)_3\}_2]$	Deep yellow	196–200				20.3	
6 $[AuCl(PPh_3)]$	White					34.0	
6a $[AuCl\{PPh_2(C_6H_4OMe\text{-}p)\}]$	White	153–154	43.76 (43.49)	3.10 (3.27)	0.00 (0.00)	32.6	
6b $[AuCl\{PPh(C_6H_4OMe\text{-}p)_2\}]$	White	92–93	44.16 (43.30)	3.43 (3.50)	0.00 (0.00)	31.3	
6c $[AuCl\{P(C_6H_4OMe\text{-}p)_3\}]$	White	155–156	43.59 (43.13)	3.49 (3.63)	0.00 (0.00)	30.0	
6f $[AuCl\{P(C_6H_4NMe_2\text{-}p)_3\}]$	White					28.3	
7 $[Mo(CO)_4(AsPh_3)_2]$	Deep yellow						2025s, 1921 (sh), 1913s, 1881 (sh)[d]
7c $[Mo(CO)_4\{As(C_6H_4OMe\text{-}p)_3\}_2]$	Deep yellow	147–148	55.12 (55.22)	4.23 (4.20)			2022s, 1919 (sh), 1909s, 1876 (sh)[d]
8 $[Fe(CO)_3(AsPh_3)_2]$	Dark yellow						2049s, 1972 (sh), 1940s[d]
8c $[Fe(CO)_4\{As(C_6H_4OMe\text{-}p)_3\}]$	Dark yellow	148–149	53.13 (53.19)	3.45 (3.72)	0.00 (0.00)		2047s, 1970 (sh), 1938s[d]

[a] Data for the known PPh_3 and $AsPh_3$ complexes restricted to ^{31}P NMR and IR. [b] Calculated values given in parentheses. [c] The ^1J(PtP) coupling constant (in Hz) is given in parentheses. [d] In CH_2Cl_2. [e] Values according to the literature.[24] [f] In CH_2Cl_2–hexane (1 : 1).

methanol there is no need to add extra acid to encourage ion formation, so the conditions for analysis are relatively mild. However, for some complexes, protic solvents may be incompatible with chemical stability. Preliminary studies show that the electrospray-friendly complexes can also be analysed in 1,2-dimethoxyethane (dme) or thf solutions with added $NaBPh_4$ as the cation source. The use of potassium salts dissolved in aprotic solvents in ESMS analyses has been reported previously.[16] Thus, analysis of compounds **1e** and **1f** in thf solution with a small quantity of added $Na[BPh_4]$ as an ionisation source yielded $[M + Na]^+$ ions as the base peaks for both compounds, at *m*/*z* 928 and 1014 respectively. The use of a more strongly co-ordinating solvent such as dme is less preferred, since this will compete with the analyte for the Na^+ ions; analysis of complex **1c** in dme gave the solvated species $[M + Na(dme)]^+$ at *m*/*z* 1026. These preliminary results suggest that the concept of electrospray-friendly ligands should be applicable to complexes with a wide range of stabilities.

The incorporation of OMe and NMe_2 groups into other types of ligands should provide a general means of facilitating mass spectrometric characterisation of complexes thereof. Thus, the bidentate phosphine $(p\text{-}MeOC_6H_4)_2CH_2CH_2P(C_6H_4\text{-}OMe\text{-}p)_2$ (L–L), when treated with $[Mo(CO)_4(pip)_2]$ (pip = piperidine), yields $[Mo(CO)_4(L\text{–}L)]$ which has not been fully characterised but gives the expected $[M + H]^+$ ion (*m*/*z* 727) as the only peak in the ESMS spectrum.

(b) Metal halide complexes. Table 3 summarises the ESMS data for metal halide complexes of the electrospray-friendly ligands. Previously, we carried out a study on a wide range of transition metal complexes which contain halide ligands, in addition to other neutral ancillary donor ligands, such as phosphines, *etc*.[6] In almost all cases, loss of a halide ligand, with solvation of the resulting cation by a solvent molecule at low cone voltages, provides the dominant ionisation pathway. For the complexes containing MeO- or NMe_2-substituted phosphine ligands, the protonation mechanism, forming $[M + H]^+$ ions, might become competitive with halide loss. However, even for the complex *cis*-$[PtCl_2\{P(C_6H_4NMe_2\text{-}p)_3\}_2]$ spectra were dominated by the ions $[M - Cl]^+$ and $[M - Cl + solvent]^+$. For the platinum complexes **4a**–**4c** the intensities of the ions appeared to depend on the number of OMe groups present. In

Table 2 Positive-ion ESMS data for the transition-metal carbonyl complexes, recorded in either MeCN–water (a) or MeOH (b) solution

Compound	Solvent	Cone voltage/V	Ions observed (*m*/*z*, %)
1a	a	20	$[M + H]^+$ (795, 100), $[M + NH_4]^+$ (812, 20)
		60	$[M + H]^+$ (795, 69), $[M + H - CO]^+$ (767, 12), $[M + H - 2CO]^+$ (739, 100), $[M + H - 3CO]^+$ (711, 48), $[M + H - 4CO]^+$ (683, 49)
		80	$[M + H]^+$ (795, 90), $[M + H - CO]^+$ (767, 19), $[M + H - 2CO]^+$ (739, 20), $[M + H - 3CO]^+$ (711, 13), $[M + H - 4CO]^+$ (683, 100)
1b	a	20	$[M + H]^+$ (855, 100), $[M + NH_4]^+$ (872, 4)
1c	b	20	$[M + H]^+$ (915, 100)
		60	$[M + H]^+$ (915, 15), $[M + H - 2CO]^+$ (859, 100), $[M + H - 3CO]^+$ (831, 41), $[M + H - 4CO]^+$ (803, 18)
1d	a	20	$[M + H]^+$ (821, 100)
1e	b	20	$[M + H]^+$ (907, 100)
1f	b	20	$[M + H]^+$ (993, 100)
2a	b	20	$[M + H]^+$ (725, 53), $[M + NH_4]^+$ (742, 100)
2b	a	20	$[M + H]^+$ (785, 100)
		60	$[M + H]^+$ (785, 100), $[M + H - 3CO]^+$ (701, 60)
		80	$[M + H]^+$ (785, 32), $[M + H - 3CO]^+$ (701, 100)
2c	a	20	$[M + H]^+$ (845, 100)
		60	$[M + H]^+$ (845, 28), $[M + H - 3CO]^+$ (761, 100)
		80	$[M + H]^+$ (845, 18), $[M + H - 3CO]^+$ (761, 100)
3a	b	20	$[M + H]^+$ (1434, 100)
		60	$[M + H]^+$ (1434, 45), $[M + H - CO]^+$ (1406, 100), $[M + H - 2CO]^+$ (1378, 36), $[M + H - 3CO]^+$ (1350, 23), $[M + H - 4CO]^+$ (1322, 12), $[M + H - 5CO]^+$ (1294, 5)
		80	$[M + H]^+$ (1434, 88), $[M + H - CO]^+$ (1406, 69), $[M + H - 2CO]^+$ (1378, 99), $[M + H - 3CO]^+$ (1350, 77), $[M + H - 4CO]^+$ (1322, 100), $[M + H - 5CO]^+$ (1294, 93), $[M + H - 6CO]^+$ (1266, 47)
3b	b	20	$[M + H]^+$ (1524, 100)
		60	$[M + H]^+$ (1524, 100), $[M + H - CO]^+$ (1496, 88), $[M + H - 2CO]^+$ (1468, 20), $[M + H - 3CO]^+$ (1440, 9), $[M + H - 4CO]^+$ (1412, 4)
3c	b	20	$[M + H]^+$ (1614, 100)
		60	$[M + H]^+$ (1614, 100), $[M + H - CO]^+$ (1586, 90), $[M + H - 2CO]^+$ (1558, 28), $[M + H - 3CO]^+$ (1530, 11), $[M + H - 4CO]^+$ (1502, 4)
		80	$[M + H]^+$ (1614, 18), $[M + H - CO]^+$ (1586, 95), $[M + H - 2CO]^+$ (1558, 63), $[M + H - 3CO]^+$ (1530, 68), $[M + H - 4CO]^+$ (1502, 100), $[M + H - 5CO]^+$ (1474, 49), $[M + H - 6CO]^+$ (1446, 9)
3d	a	20	$[M + H]^+$ (1473, 100), $[M + Na]^+$ (1495, 10)
		60	$[M + H]^+$ (1473, 25), $[M + H - CO]^+$ (1445, 92), $[M + H - 2CO]^+$ (1417, 100), $[M + H - 3CO]^+$ (1389, 69), $[M + H - 4CO]^+$ (1361, 56), $[M + H - 5CO]^+$ (1333, 29)
		80	$[M + H]^+$ (1473, 18), $[M + H - CO]^+$ (1445, 29), $[M + H - 2CO]^+$ (1417, 50), $[M + H - 3CO]^+$ (1389, 14), $[M + H - 4CO]^+$ (1361, 40), $[M + H - 5CO]^+$ (1333, 79), $[M + H - 6CO]^+$ (1305, 100)
3e	a	20	$[M + H]^+$ (1602, 100), $[M + Na]^+$ (1624, 29)
		60	$[M + H]^+$ (1602, 70), $[M + Na]^+$ (1624, 20), $[M + H - CO]^+$ (1574, 100), $[M + H - 2CO]^+$ (1546, 65), $[M + H - 3CO]^+$ (1518, 30), $[M + H - 4CO]^+$ (1490, 27)
		80	$[M + H]^+$ (1602, 59), $[M + H - CO]^+$ (1574, 48), $[M + H - 2CO]^+$ (1546, 68), $[M + H - 3CO]^+$ (1518, 35), $[M + H - 4CO]^+$ (1490, 78), $[M + H - 5CO]^+$ (1362, 79), $[M + H - 6CO]^+$ (1434, 100)
3f	a	20	$[M + H]^+$ (1731, 100), $[M + Na]^+$ (1753, 30)
		60	$[M + H]^+$ (1731, 100), $[M + Na]^+$ (1753, 16), $[M + H - CO]^+$ (1703, 65), $[M + H - 2CO]^+$ (1675, 20), $[M + H - 3CO]^+$ (1647, 8), $[M + H - 4CO]^+$ (1619, 8), $[M + H - 5CO]^+$ (1582, 8), $[M + H - 6CO]^+$ (1552, 10)
7c	a	20	$[M + H]^+$ (1003, 100)
8c	a	20	$[M + H]^+$ (564, 100)

m/*z* values quoted represent the peak of greatest intensity in the isotope distribution pattern of that ion, verified with a simulated isotope pattern.

the gold compounds **6** and **6a**–**6c** the bis(phosphine)gold cation $[L_2Au]^+$ dominated both the high and low cone voltage spectra, but smaller solvated $[M - Cl + MeCN]^+$ ions were seen. This behaviour is typical for gold(I) phosphine complexes which tend to be labile in solution.[17] For complex **6f** the base peak was interestingly the ammonia-containing ion $[M - Cl + NH_3]^+$, though the bis(phosphine)gold cation was still observed.

Dilute HCl was added to try and suppress the loss of chloride from the platinum centre in complexes **4a**–**4f**, and to promote protonation, however the spectra were basically unchanged, with the exception that the $[M - Cl + NH_3]^+$ ions observed in MeCN–water solution had disappeared. No $[M + H]^+$ ions were observed. Addition of pyridine to the analyte solution resulted in observation of the expected $[M - Cl + py]^+$ ions, as observed previously.[6] Thus, the use of electrospray-friendly ligands appears to offer no advantages over the simple triphenylphosphine, when ionisable halide ligands are present in the complex.

Conclusion

The OMe and NMe_2 substituted triphenylphosphines, and the arsine $As(C_6H_4OMe\text{-}p)_3$ appear to be good ligands for the ESMS characterisation of neutral transition metal complexes, especially carbonyls (and other complexes without labile anionic ligands) where the analogous PPh_3 or $AsPh_3$ compounds are invisible. The NMR and IR studies confirm that the electrospray-friendly ligands are similar to the parent PPh_3 and $AsPh_3$ ligands. For complexes which contain a halide ligand, loss of this halide remains the dominant ionisation pathway. A single OMe group appears to be sufficient to allow analysis by ESMS, but greater ionisation efficiency is achieved by higher numbers of OMe groups, and particularly by the use of the more basic NMe_2 group. The use of these ligands may play a very useful role in transition metal chemistry, allowing the detection of products and intermediates not previously characterised. In this respect, the ability to sample directly from

Table 3 Positive-ion ESMS data[a] for the transition-metal halide complexes, recorded in MeCN–water solution at a cone voltage of 20 V

Compound	Ions observed (*m/z*, %)[b]
4a	$[M - Cl + MeCN]^+$ (856, 100), $[M - Cl + NH_3]^+$ (832, 9), $[M - Cl]^+$ (815, 52)
4b	$[M - Cl + MeCN]^+$ (916, 99), $[M - Cl]^+$ (875, 100)
4c	$[M - Cl + MeCN]^+$ (976, 30), $[M - Cl + NH_3]^+$ (952, 10), $[M - Cl]^+$ (935, 100)
4f	$[M - Cl + NH_3]^+$ (1030, 100), $[M - Cl]^+$ (1013, 84)
5a	$[M - Cl + MeCN]^+$ (766/768, 40), $[M - Cl + NH_3]^+$ (742/744, 18), $[M - Cl]^+$ (725/727, 100)
5b	$[M - Cl + MeCN]^+$ (826/828, 26), $[M - Cl + NH_3]^+$ (802/804, 13), $[M - Cl]^+$ (785/787, 100)
5c	$[M - Cl]^+$ (845/847, 100)
6a	$[L_2Au]^+$ (781, 100), $[M - Cl + MeCN]^+$ (530, 7)
6b	$[L_2Au]^+$ (841, 100), $[M - Cl + MeCN]^+$ (560, 8)
6c	$[L_2Au]^+$ (901, 100), $[M - Cl + MeCN]^+$ (590, 18)
6f	$[L_2Au]^+$ (979, 15), $[M - Cl + MeCN]^+$ (629, 50), $[M - Cl + NH_3]^+$ (605, 100)

[a] *m/z* values quoted represent the peak of greatest intensity in the isotope distribution pattern of that ion, verified with a simulated isotope pattern. [b] M refers to the parent complex, L to the phosphine ligand therein.

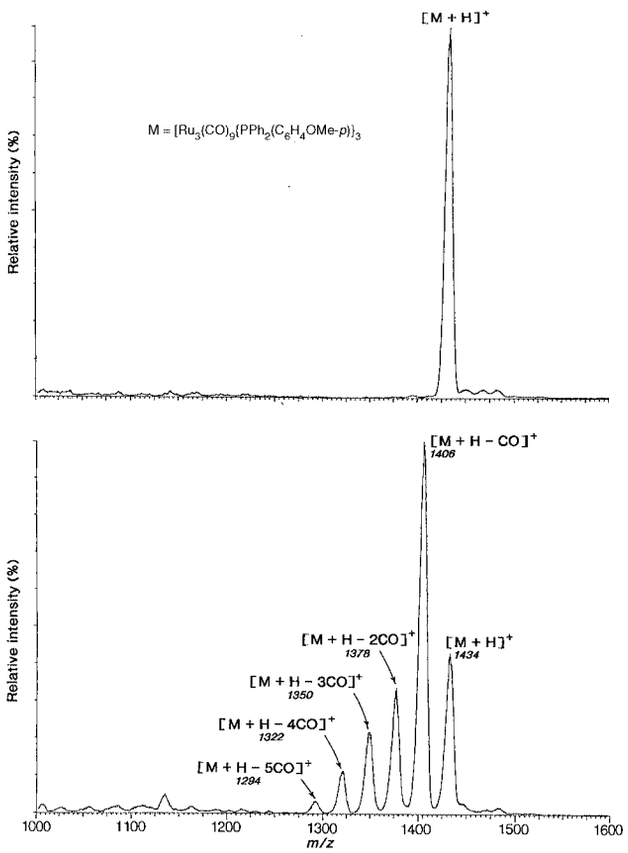

Fig. 1 Positive-ion ES spectra of $[Ru_3(CO)_9\{PPh_2(C_6H_4OMe\text{-}p)\}_3]$ **3a** in methanol, at cone voltages of 20 (upper spectrum) and 60 V (lower spectrum), showing the assignment of the ions.

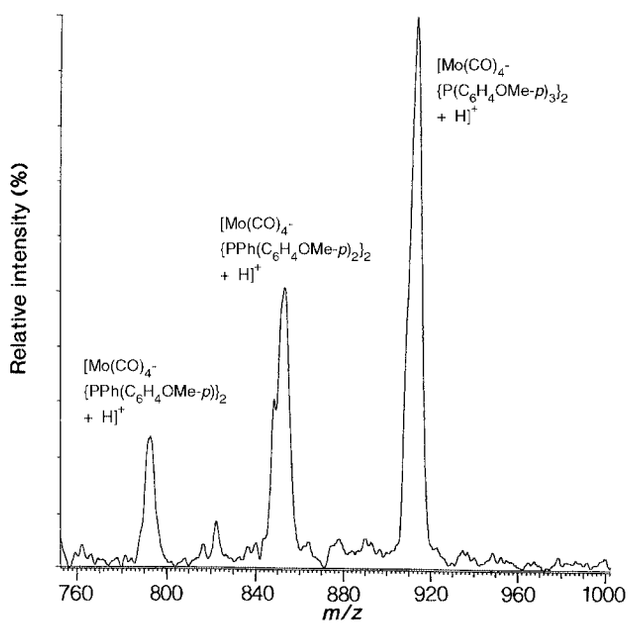

Fig. 2 Positive-ion ES spectrum of a 1:1:1 molar mixture of $[Mo(CO)_4\{PPh_2(C_6H_4OMe\text{-}p)\}_2]$ **1a**, $[Mo(CO)_4\{PPh(C_6H_4OMe\text{-}p)_2\}_2]$ **1b** and $[Mo(CO)_4\{P(C_6H_4OMe\text{-}p)_3\}_2]$ **1c** in methanol solution, at a cone voltage of 20 V, showing the increased ionisation efficiency with increased numbers of OMe groups.

reaction solutions carried out on a very small scale is a major advantage of ESMS over other methods of monitoring. Assignment of peaks is simplified by the lack of fragmentation of parent ions, compared with other MS techniques.

Experimental

Unless otherwise specified, all reactions were performed under a dinitrogen atmosphere using standard Schlenk techniques. The solvents dichloromethane and light petroleum (bp 40–60 °C) were distilled from calcium hydride, tetrahydrofuran and diethyl ether from sodium–benzophenone. Other reagent grade solvents were used without purification.

Melting points were recorded on a Reichert Thermopan apparatus and are uncorrected. Infrared spectra were obtained in solution on a BioRad FTS-40 instrument, and ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra on a Bruker AC300P spectrometer at 300.13, 75.47 and 121.5 Hz respectively. All NMR spectra were recorded in $CDCl_3$ solution, ^1H and ^{13}C referenced to residual $CHCl_3$ and ^{31}P to an external standard of 85% H_3PO_4. Elemental microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago.

Electrospray mass spectra were recorded in positive-ion mode on a VG Platform II mass spectrometer. Compounds were dissolved in 1:1 v/v acetonitrile–water or methanol and injected directly *via* a Rheodyne injector with a 10 μl sample loop. A SpectraPhysics isocratic LC Spectra System P1000 pump delivered the solution (typically 1 mg mL^{-1}) at 0.02 ml min^{-1} to the mass spectrometer source (60 °C), and nitrogen was employed both as a drying and nebulising gas. Skimmer cone voltages were varied between 20 and 80 V, in order to investigate the effects of higher cone voltages on fragmentation of the parent ions. Theoretical isotope distribution patterns were calculated using the ISOTOPE computer program[18] and used to aid in assignment. Peaks in the mass spectra are listed in Tables 2 and 3 by the most intense *m/z* value in the isotopic mass distribution.

The phosphine ligands $PPh_2(C_6H_4OMe\text{-}p)$, $PPh(C_6H_4OMe\text{-}p)_2$ and $P(C_6H_4OMe\text{-}p)_3$ were prepared as reported by Schiemenz.[19] The other ligands were prepared following the

same general procedure. The preparations of $PPh_2(C_6H_4NMe_2$-*p*),[20] $PPh(C_6H_4NMe_2$-*p*$)_2$[21] and $P(C_6H_4NMe_2$-*p*$)_3$[20] have been reported before. Complexes **1**,[22] **2**,[23] **3**,[24] **4f**[20] and **6**[25] were prepared by the published methods. The complexes $[PtCl_2(cod)]$[26] and $[PdCl_2(cod)]$[27] (cod = 1,5-cyclooctadiene) were prepared by the literature procedures, and the phosphine complexes formed from them by ligand displacement.[28] The complexes $[Mo(CO)_4(pip)_2]$[22] (pip = piperidine) and $HAuCl_4$[29] were prepared by the literature procedures. The compound $PhPCl_2$, Ph_2PCl, $[Ru_3(CO)_{12}]$ and $[Fe(CO)_5]$ (Strem Chemicals), *p*-bromoanisole and *p*-bromo-*N*,*N*-dimethylaniline (Aldrich), PCl_3 and PPh_3 (BDH) were used as supplied.

Syntheses

$PPh(C_6H_4NMe_2$-*p*$)_2$. A solution of the Grignard $BrMgC_6H_4NMe_2$-*p* was prepared from Mg (1.04 g, 43.2 mmol) and *p*-bromo-*N*,*N*-dimethylaniline (8.64 g, 43.2 mmol) in thf (40 mL). A solution of $PhPCl_2$ (2.53 g, 1.95 mL; 14.4 mmol) in thf (40 mL) was added slowly at 0 °C. The reaction mixture was refluxed for 1 h, cooled to room temperature and hydrolysed with strong (*ca.* 10%) NH_4Cl solution at 0 °C. The phosphine was then extracted with toluene (3 × 100 mL), evaporated to dryness under reduced pressure and recrystallised from methanol. Yield: 4.00 g, 80%.

$As(C_6H_4OMe$-*p*$)_3$. Using the same method as above, the Grignard from Mg (907 mg, 37.8 mmol), and *p*-bromoanisole (7.07 g, 4.7 mL; 37.8 mmol) was treated with $AsCl_3$ (2.27 g, 1.1 mL; 12.6 mmol) to give $As(C_6H_4OMe$-*p*$)_3$ (3.2 g, 64%).

$[Mo(CO)_4\{PPh_2(C_6H_4OMe$-*p*$)\}_2]$ 1a. The complex $[Mo(CO)_4(pip)_2]$ (95 mg, 0.25 mmol) was partially dissolved in CH_2Cl_2 (10 mL) and $PPh_2(C_6H_4OMe$-*p*) (146 mg, 0.5 mmol) added. The reaction mixture was heated to reflux whereupon the $[Mo(CO)_4(pip)_2]$ fully dissolved. Reflux was maintained for 15 min. The reaction solution was allowed to cool to room temperature and the orange solution filtered. The filtrate was reduced in volume to *ca*. 4 mL (rotary evaporator) and methanol (10 mL) added. The solution was cooled in a freezer overnight and the pale yellow product crystallised. It was collected by filtration and air dried. The complex was purified by dissolving in hot methanol, and crystallising at −20 °C. Yield 202 mg, 81%.

Similarly prepared were: $[Mo(CO)_4\{PPh(C_6H_4OMe$-*p*$)\}_2]$ **1b**, from $[Mo(CO)_4(pip)_2]$ (132 mg, 0.35 mmol) and $PPh(C_6H_4OMe$-*p*$)_2$ (225 mg, 0.7 mmol), yield 261 mg (87%); $[Mo(CO)_4\{P(C_6H_4OMe$-*p*$)_3\}_2]$ **1c**, from $[Mo(CO)_4(pip)_2]$ (144 mg, 0.38 mmol) and $P(C_6H_4OMe$-*p*$)_3$ (268 mg, 0.76 mmol), yield 242 mg (69%); $[Mo(CO)_4\{PPh_2(C_6H_4NMe_2$-*p*$)\}_2]$ **1d**, from $[Mo(CO)_4(pip)_2]$ (312 mg, 0.825 mmol) and $PPh_2(C_6H_4NMe_2$-*p*) (500 mg, 1.65 mmol), yield 415 mg (62%); $[Mo(CO)_4\{PPh(C_6H_4NMe_2$-*p*$)\}_2]$ **1e**, from $[Mo(CO)_4(pip)_2]$ (272 mg, 0.72 mmol) and $PPh(C_6H_4NMe_2$-*p*$)_2$ (500 mg, 1.44 mmol), yield 507 mg (78%); $[Mo(CO)_4\{P(C_6H_4NMe_2$-*p*$)_3\}_2]$ **1f**, from $[Mo(CO)_4(pip)_2]$ (242 mg, 0.64 mmol) and $P(C_6H_4NMe_2$-*p*$)_3$ (500 mg, 1.28 mmol), yield 258 mg (41%); $[Mo(CO)_4(AsPh_3)_2]$ **7**, from $[Mo(CO)_4(pip)_2]$ (150 mg, 0.4 mmol) and $AsPh_3$ (245 mg, 0.8 mmol), yield 190 mg (58%); $[Mo(CO)_4\{As(C_6H_4OMe$-*p*$)_3\}_2]$ **7c**, from $[Mo(CO)_4(pip)_2]$ (150 mg, 0.4 mmol) and $As(C_6H_4OMe$-*p*$)_3$ (317 mg, 0.8 mmol), yield 114 mg (29%).

$[Fe(CO)_3\{PPh_2(C_6H_4OMe$-*p*$)\}_2]$ 2a. The reaction was carried out following a modification of the literature procedure for complex **2**[23] with $[Fe(CO)_5]$ (0.1 mL, 0.149 g, 0.76 mmol), $PPh_2(C_6H_4OMe$-*p*) (0.467 g, 1.6 mmol) and $NaBH_4$ (0.059 g, 1.53 mmol). The $NaBH_4$ was placed in the reaction flask, followed by 20 ml of ethanol. The solution was purged with nitrogen for 20 min and the phosphine ligand added. Pentacarbonyliron(0) was then added dropwise by a syringe. Precipitation began during the course of the reaction. After cooling, the reaction mixture was placed in a freezer for 12 h. The precipitate was collected by filtration and washed with CH_3OH (3 × 5 mL). The complex was purified by dissolving the product in CH_2Cl_2 (5 mL) and filtering it into a flask containing 10 mL of ice-cold CH_3OH. The precipitate and solution were cooled to 5 °C for 12 h. The product was collected by filtration, washed with three 5 mL portions of ice-cold CH_3OH, and dried under vacuum. Yield: 78 mg, 39%.

The following were prepared similarly: $[Fe(CO)_3\{PPh(C_6H_4OMe$-*p*$)_2\}]$ **2b**, from $[Fe(CO)_5]$ (0.1 mL, 0.149 g, 0.76 mmol), $PPh(C_6H_4OMe$-*p*$)_2$ (0.515 g, 1.6 mmol) and $NaBH_4$ (0.058 g, 0.53 mmol), yield 92 mg (46%); $[Fe(CO)_3\{P(C_6H_4OMe$-*p*$)_3\}_2]$ **2c**, from $[Fe(CO)_5]$ (0.1 mL, 0.149 g, 0.76 mmol), $P(C_6H_4OMe$-*p*$)_3$ (0.563 g, 1.6 mmol) and $NaBH_4$ (0.058 g, 0.53 mmol), yield 71 mg (36%); previously by alternative methods;[30] $[Fe(CO)_3(AsPh_3)_2]$ **8**, from $[Fe(CO)_5]$ (0.53 mL, 0.078 g, 0.4 mmol), $AsPh_3$ (0.245 g, 0.8 mmol) and $NaBH_4$ (0.03 g, 0.8 mmol), yield 150 mg (50%); $[Fe(CO)_4\{As(C_6H_4OMe$-*p*$)_3\}]$ **8c**, from $[Fe(CO)_5]$ (0.53 mL, 0.078 g, 0.4 mmol), $As(C_6H_4OMe$-*p*$)_3$ (0.317 g, 0.8 mmol) and $NaBH_4$ (0.03 g, 0.8 mmol), yield 85 mg (23%); analysis of the crude reaction mixture showed a mixture of the mono- and di-substituted products.

$[Ru_3(CO)_9\{PPh_2(C_6H_4OMe$-*p*$)\}_3]$ 3a. This complex was prepared by a modification of the literature procedure.[24] A solution of $[Ru_3(CO)_{12}]$ (61 mg, 0.14 mmol) and $PPh_2(C_6H_4OMe$-*p*) (123 mg, 0.42 mmol) in toluene (5 mL) was refluxed for 30 min. The pure product was obtained by chromatography on silica, eluting with light petroleum–CH_2Cl_2 (1 : 4). Yield: 160 mg, 80%.

The following complexes were similarly prepared: $[Ru_3(CO)_9\{PPh(C_6H_4OMe$-*p*$)_2\}_3]$ **3b**, from $[Ru_3(CO)_{12}]$ (85.5, 0.20 mmol) and $PPh(C_6H_4OMe$-*p*$)_2$ (190 mg, 0.60 mmol), yield 218 mg (73%); $[Ru_3(CO)_9\{P(C_6H_4OMe$-*p*$)_3\}_3]$ **3c**, from $[Ru_3(CO)_{12}]$ (54 mg, 0.124 mmol) and $P(C_6H_4OMe$-*p*$)_3$ (131 mg, 0.372 mmol), yield 172 mg (86%); $[Ru_3(CO)_9\{PPh_2(C_6H_4NMe_2$-*p*$)\}_3]$ **3d**, from $[Ru_3(CO)_{12}]$ (29 mg, 0.066 mmol) and $PPh_2(C_6H_4NMe_2$-*p*) (60 mg, 0.20 mmol), yield 53 mg (53%); $[Ru_3(CO)_9\{PPh(C_6H_4NMe_2$-*p*$)_2\}_3]$ **3e**, from $[Ru_3(CO)_{12}]$ (22 mg, 0.05 mmol) and $PPh(C_6H_4NMe_2$-*p*$)_2$ (50 mg, 0.14 mmol), yield 39 mg (49%); $[Ru_3(CO)_9\{P(C_6H_4NMe_2$-*p*$)_3\}_3]$ **3f**, from $[Ru_3(CO)_{12}]$ (29 mg, 0.066 mmol) and $P(C_6H_4NMe_2$-*p*$)_3$ (78 mg, 0.20 mmol), yield 39 mg (34%).

***cis*-$[PtCl_2(PPh_3)_2]$ 4.** Without regard for exclusion of air, PPh_3 (142 mg, 0.54 mmol) was added to a dichloromethane solution (5 mL) of $[PtCl_2(cod)]$ (100 mg, 0.27 mmol). The reaction mixture was stirred at room temperature for 10 min. Addition of light petroleum induced precipitation of **4** (164 mg, 77%), which was filtered off and washed with diethyl ether.

The following complexes were prepared similarly: *cis*-$[PtCl_2\{PPh_2(C_6H_4OMe$-*p*$)\}_2]$ **4a**, $PPh_2(C_6H_4OMe$-*p*) (158 mg, 0.54 mmol) and $[PtCl_2(cod)]$ (100 mg, 0.27 mmol) gave 152 mg (66%); *cis*-$[PtCl_2\{PPh(C_6H_4OMe$-*p*$)_2\}_2]$ **4b**, $PPh(C_6H_4OMe$-*p*$)_2$ (174 mg, 0.54 mmol) and $[PtCl_2(cod)]$ (100 mg, 0.27 mmol) gave 198 mg (80.5%); *cis*-$[PtCl_2\{P(C_6H_4NMe_2$-*p*$)_3\}_2]$ **4f**, $P(C_6H_4NMe_2$-*p*$)_3$ (211 mg, 0.54 mmol) and $[PtCl_2(cod)]$ (100 mg, 0.27 mmol) gave 105 mg (39%); $[PdCl_2(PPh_3)_2]$ **5**, PPh_3 (183 mg, 0.7 mmol) and $[PdCl_2(cod)]$ (100 mg, 0.35 mmol) gave 225 mg (92%); $[PdCl_2\{PPh_2(C_6H_4OMe$-*p*$)\}_2]$ **5a**, $PPh_2(C_6H_4OMe$-*p*) (204 mg, 0.7 mmol) and $[PdCl_2(cod)]$ (100 mg, 0.35 mmol) gave 106 mg (40%); $[PdCl_2\{PPh(C_6H_4OMe$-*p*$)_2\}_2]$ **5b**, $PPh(C_6H_4OMe$-*p*$)_2$ (225 mg, 0.7 mmol) and $[PdCl_2(cod)]$ (100 mg, 0.35 mmol) gave 170 mg (60%); this complex has been reported previously;[31] $[PdCl_2\{P(C_6H_4OMe$-*p*$)_3\}_2]$ **5c**, $P(C_6H_4OMe$-*p*$)_3$ (246 mg, 0.7 mmol) and $[PdCl_2(cod)]$ (100 mg, 0.35 mmol) gave 200 mg (65%).

$[AuCl\{PPh_2(C_6H_4OMe$-*p*$)\}]$ 6a. Without regard for the exclusion of air, $PPh_2(C_6H_4OMe$-*p*) (172 mg, 0.59 mmol) was added to an ethanol solution (5 mL) of $HAuCl_4$ (100 mg, 0.29 mmol).

The reaction mixture was stirred at room temperature for 10 min. Addition of several mL of water induced precipitation of complex **6a**. The solution was cooled in a refrigerator overnight and the product was filtered off and dried (63 mg, 41%). An analytically pure sample was prepared by recrystallisation from hot methanol.

The following complexes were prepared similarly: [AuCl{$PPh(C_6H_4OMe\text{-}p)_2$}] **6b**, $PPh(C_6H_4OMe\text{-}p)_2$ (189 mg, 0.59 mmol) and $HAuCl_4$ (100 mg, 0.29 mmol) gave 74 mg (45%); [AuCl{$P(C_6H_4OMe\text{-}p)_3$}] **6c**, $P(C_6H_4OMe\text{-}p)_3$ (207 mg, 0.59 mmol) and $HAuCl_4$ (100 mg, 0.29 mmol) gave 154 mg (90%); [AuCl{$P(C_6H_4NMe_2\text{-}p)_3$}] **6f**, $P(C_6H_4NMe_2\text{-}p)_3$ (227 mg, 0.58 mmol) and $HAuCl_4$ (100 mg, 0.29 mmol) gave 95 mg (53%), reported previously by a different route.[32]

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