Some Square-planar Alkoxo- and Hydroxo-complexes of Group 8: Preparation, Bonding, and Novel Condensation Reactions with Active Methyl Compounds

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A series of mononuclear methoxo-complexes, *cis*- and *trans*-$[MR(OMe)(PPh_3)_2]$ (M = Pd or Pt; R = aryl or alkenyl) has been prepared by metathesis of $[MR(Cl)(PPh_3)_2]$ with Na(OMe). Hydrolysis of the methoxo-complexes gives corresponding hydroxo-complexes, *trans*-$[MR(OH)(PPh_3)_2]$, which are also obtained from $[MR(OCMe_2)(PPh_3)_2]^+$ and $[OH]^-$. The stability and nature of the M–OR bond (R = H or Me) are influenced markedly by the identity of the metal and the *trans* ligand, R. The anionic character of the OH or OR ligand increases in the orders Pt < Pd and C_6F_5 < CCl=CCl$_2$ < CH=CCl$_2$ < Ph. The hydroxo-complexes react with PhCOMe and MeNO$_2$ to give the corresponding condensates, *trans*-$[PtR(CH_2X)(PPh_3)_2]$ (X = COPh or NO$_2$). The condensation reaction is facilitated by the increase in anionic character of the OH ligand.

The chemistry of hydroxo- and alkoxo-complexes of the later transition metals is of interest because of the potent reactivity anticipated and the possibility for application to organic synthesis. Intermediacy of hydroxopalladium complexes has been postulated in the Wacker process.[1] In platinum(II)-catalysed hydration of nitriles, hydroxo-complexes doubtless play an important role.[2] An alkoxo-complex of palladium(II) was believed to be involved in vinyl exchange reactions of vinyl ethers.[3] While some non-bridging hydroxo-complexes of d^8 metals such as Ru^0,[4] Os^0,[4] Rh^I,[5] Ir^I,[6-9] Pd^{II},[10] and Pt^{II} (refs. 11—14) have been isolated, only two alkoxo-complexes of these 'soft' metals are known, *i.e.* $[Pt(C_6H_9)(OMe)(dppe)]$[12] (C_6H_9 = cyclohexenyl, dppe = $Ph_2PCH_2CH_2PPh_2$) and $[Ir(NO)(OR)(PPh_3)_2]^+$ (R = Et or Pr^n).[6] In order to elucidate factors governing the reactivity of M–OH or M–OR bonds, a series of square-planar complexes, *cis*- and *trans*-$[M(R')(OR)(PPh_3)_2]$ (M = Pd or Pt; R = H or Me; R' = aryl or alkenyl), has been prepared. This paper describes the preparation and spectral data relevant to a discussion of the bonding with reference to the identity of the metal and the properties of auxiliary ligands, in particular the ligand which is *trans* to OH or OR. A novel condensation reaction is also described between hydroxo-complexes and organic compounds containing an active methyl group, which yields alkyl complexes.

RESULTS AND DISCUSSION

Preparation.—The methoxo-complexes $[MR(OMe)(PPh_3)_2]$ (M = Pd or Pt) were prepared by a simple metathesis reaction of $[MR(Cl)(PPh_3)_2]$ with Na(OMe). For example, on treating *cis*-$[Pt(C_6F_5)(Cl)(PPh_3)_2]$ with an excess of Na(OMe) in a mixture of methanol and toluene at 60 °C, colourless *cis*-$[Pt(C_6F_5)(OMe)(PPh_3)_2]$, (I; R = C_6F_5), was obtained. Similarly *cis*-$[Pt(CCl{=}CCl_2)(Cl)(PPh_3)_2]$ and *trans*-$[Pt(CH{=}CCl_2)(Cl)(PPh_3)_2]$ give the corresponding methoxo-complexes, *cis*-$[Pt(CCl{=}CCl_2)(OMe)(PPh_3)_2]$, (I; R = CCl=CCl$_2$), and *trans*-$[Pt(CH{=}CCl_2)(OMe)(PPh_3)_2]$, (II; R = CH=CCl$_2$), respectively. An attempt to prepare the monochlorovinyl analogue from *trans*-$[Pt(CH{=}CHCl)(Cl)(PPh_3)_2]$ and Na(OMe) failed, uncharacterised amorphous brown solids being formed.

Similar displacement of a halide ligand in *trans*-$[PdR(Cl)(PPh_3)_2]$ (R = C_6F_5 or CCl=CCl$_2$) with Na(OMe) at 40 °C gave pale yellow *trans*-$[PdR(OMe)(PPh_3)_2]$ (III; R = C_6F_5 or CCl=CCl$_2$). Higher temperatures reduced the yield. Formation of (III; R = CCl=CCl$_2$) was accompanied by a trace amount of a hydride complex derived from β-hydrogen elimination in (III). The instability and extremely low yield of the hydride prevented isolation of an analytically pure sample. The ^{1}H n.m.r. (δ –7.62 p.p.m.) and i.r. spectra [ν(Pd–H) at 1 866 cm^{-1}] support the formulation as *trans*-$[Pd(CCl{=}CCl_2)H(PPh_3)_2]$, since a hydride ligand *trans* to a ligand of high *trans* influence gives rise to an n.m.r. signal at low field, indicative of enhanced deshielding, and a low metal–hydride stretching frequency, *e.g.* *trans*-$[Pt(C_6H_9)H(PPh_3)_2]$[12] [δ –4.64 p.p.m., ν(Pt–H) at 1 920 cm^{-1}] and *trans*-$[PtH_2(PBu^t_2Ph)_2]$[15] (δ –3.05 p.p.m., ν(Pt–H) at 1 740 cm^{-1}].

The success in preparing *trans*-$[MR(OMe)(PPh_3)_2]$ from the corresponding chloro-complex depends on the nature of the *trans* ligand. Thus, reaction of *trans*-$[Pd(CH{=}CCl_2)(Cl)(PPh_3)_2]$ with Na(OMe) at 35 °C in toluene did not produce the expected methoxo-complex; instead, $[\{Pd(PPh_3)_2\}_n]$ was obtained which gives

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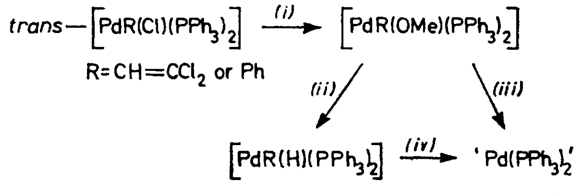
$[Pd(PPh_3)_4]$ on addition of 2 mol of PPh_3. The compounds $CCl_2{=}CH_2$ and HCHO were detected in the reaction mixture by vapour-phase chromatography (v.p.c.). Similarly, *trans*-$[PdBr(C_6H_5)(PPh_3)_2]$ gave benzene (80% yield), HCHO (*ca.* 20% yield), and anisole (trace). The formation of $[\{Pd(PPh_3)_2\}_n]$ may be accounted for by β-hydrogen elimination in the methoxo-ligand in the initial product *trans*-$[PdR(OMe)(PPh_3)_2]$ ($R = CH{=}CCl_2$ or Ph) giving HCHO and $[PdR(H)(PPh_3)_2]$ which subsequently undergoes reductive elimination of RH. A closely related reaction is formation of butane from $[PtH(Cl)(PEt_3)_2]$ and $LiBu^n$.[16] The species '$Pd(PPh_3)_2$' could also be formed directly from *trans*-$[PdPh(OMe)(PPh_3)_2]$ together with the coupling product anisole.

TABLE 1

Elemental analyses and some properties

Complex	M.p.[a] (θ_c/°C)	Colour	Analysis[b]/% C	H	Cl
cis-$[Pt(C_6F_5)(OMe)(PPh_3)_2]$ (I)	193	Colourless	56.6 (56.2)	2.9 (3.6)	
cis-$[Pt(CCl{=}CCl_2)(OMe)(PPh_3)_2]$ (I)	213	Colourless	53.2 (53.2)	3.7 (3.8)	12.1 (12.1)
trans-$[Pt(CH{=}CCl_2)(OMe)(PPh_3)_2]$ (II)	170	Colourless	55.1 (55.3)	3.8 (4.1)	8.5 (8.4)
trans-$[Pd(C_6F_5)(OMe)(PPh_3)_2]$ (III)	110	Pale yellow	62.5 (62.2)	3.7 (4.0)	
trans-$[Pd(CCl{=}CCl_2)(OMe)(PPh_3)_2]$ (III)[c]	115	Pale yellow	58.9 (59.1)	3.9 (4.2)	13.5 (13.4)
$[\{Ni(C_6F_5)(\mu\text{-}OMe)(PPh_3)\}_2]$ (IV)	155	Red	59.2 (57.5)	3.4 (3.5)	
$[\{Ni(CCl{=}CCl_2)(\mu\text{-}OMe)(PPh_3)\}_2]$ (V)[e]	125	Red	52.2 (52.3)	3.5 (3.8)	21.6 (22.1)
cis-$[Pt(C_6F_5)(OH)(PPh_3)_2]$ (VIII)	185	Colourless	55.8 (55.9)	3.4 (3.5)	
trans-$[Pt(CCl{=}CCl_2)(OH)(PPh_3)_2]$ (VI)[f]	210	Colourless	52.9 (52.6)	3.6 (3.6)	12.1 (12.3)
trans-$[Pt(CH{=}CCl_2)(OH)(PPh_3)_2]$ (VI)	230	Colourless	54.3 (54.8)	3.8 (3.9)	9.1 (8.5)
trans-$[PtPh(OH)(PPh_3)_2]$ (VI)	175	Colourless	61.8 (62.0)	4.5 (4.5)	
$[PtMe(OH)(PPh_3)_2]$ (IX)	155	Colourless	58.3 (59.1)	4.4 (4.6)	
trans-$[Pd(C_6F_5)(OH)(PPh_3)_2]$ (VII)	180	Colourless	60.6 (61.8)	4.0 (3.8)	
trans-$[Pd(CCl{=}CCl_2)(OH)(PPh_3)_2]$ (VII)[g]	100	Colourless	58.9 (58.6)	4.0 (4.0)	13.7 (13.7)
$[\{Ni(CCl{=}CCl_2)(\mu\text{-}OH)(PPh_3)\}_2]$ (X)	80	Orange	51.4 (51.3)	3.4 (3.4)	22.7 (22.7)
trans-$[Pt(CCl{=}CCl_2)(CH_2NO_2)(PPh_3)_2]$ (XI)[h]	210	Colourless	51.3 (51.5)	3.6 (3.5)	11.7 (11.7)
trans-$[Pt(CH{=}CCl_2)(CH_2NO_2)(PPh_3)_2]$ (XI)[i]	240	Colourless	54.5 (53.5)	3.9 (3.8)	8.3 (8.1)
trans-$[PtPh(CH_2NO_2)(PPh_3)_2]$ (XI)[j]	200	Colourless	59.9 (60.3)	4.3 (4.4)	
trans-$[PtPh(CH_2COPh)(PPh_3)_2]$ (XII)	195	Colourless	65.6 (65.6)	4.7 (4.6)	
$[PtMe(CH_2COPh)(PPh_3)_2]$ (XIII)	175	Colourless	63.1 (63.3)	4.7 (4.7)	

[a] With decomposition in air. [b] Calculated values are given in parentheses. [c] *M*, 760[d] (calc.: 792). [d] Cryoscopy in benzene. [e] *M*, 913[d] (calc.: 965). [f] *M*, 778[d] (calc.: 836). [g] *M*, 798[d] (calc.: 757). [h] N, 1.60 (calc.: 1.55%). [i] N, 1.45 (calc.: 1.60%) [j] N, 1.55 (calc.: 1.65%).

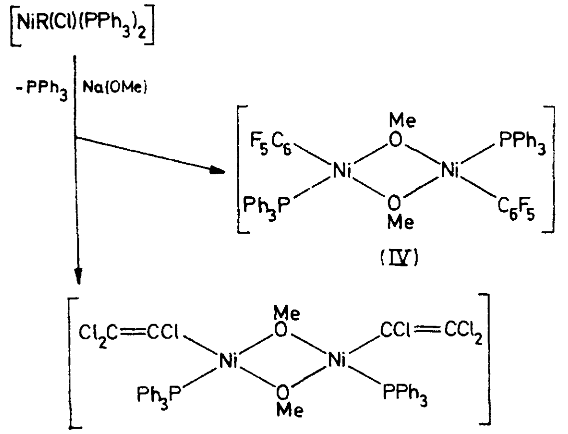


SCHEME (*i*), Na(OMe); (*ii*), —HCHO; (*iii*), —PhCOMe; (*iv*), —RH

In contrast to platinum and palladium complexes, (I)—(III), the reaction of $[NiR(Cl)(PPh_3)_2]$ with Na(OMe) gave μ-methoxo-complexes $[\{NiR(\mu\text{-}OMe)(PPh_3)\}_2]$ (IV, $R = C_6F_5$; V, $R = CCl{=}CCl_2$) as red crystals with dissociation of 1 mol of PPh_3. This type of methoxo- and hydroxo-complex of nickel has been noted previously.[17]

Platinum complexes (I) and (II) are thermally stable and air stable and can be stored at room temperature for months under nitrogen, whereas the palladium complexes (III) are less thermally stable and gradually decompose even in the solid state. The binuclear nickel complexes are extremely thermally unstable and are air sensitive even in the solid state. Methoxo-complexes (I)—(III) are soluble in aromatic hydrocarbons, but insoluble in saturated hydrocarbons, and nickel complexes (IV) and (V) are soluble in n-hexane. Complexes (I)—(V) resist β-hydrogen elimination and do not form corresponding hydride complexes on prolonged heating in benzene.

The stereochemistry of the complexes is readily deducible from their ^1H n.m.r. spectra (Table 2). Thus the methoxo-proton signals of *cis* complexes, (I), were observed as a doublet, due to the strong coupling only with the *trans*-phosphorus atom, accompanied by platinum-195 satellite bands. The values for ^4J[HP(*trans*)] and ^3J(HPt) are comparable with the respective value for $[Pt(C_6H_9)(OMe)(dppe)]$ [11] {^4J[HP(*trans*)] 5.6,



(IV)

(V)

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^3J(HPt) 52 Hz} for which ^4J[HP(*cis*)] is negligibly small. The singlet signal observed for the methoxo-protons of *trans* complexes (II) indicates a very small coupling with the *cis*-phosphorus atoms. The magnitude of ^3J(HPt) for (II) is only half those for the *cis* complexes. The palladium complexes, (III), are *trans* since their methoxo-proton signals were observed as a triplet {^4J[HP(*cis*)] 1.8 (R = C_6F_5) and 1.4 Hz (R = $CCl{=}CCl_2$)}.

The nickel complex, (V), showed two methoxo-proton signals at δ 2.16 (sharp singlet) and 2.26 p.p.m. (broad) of equal intensity suggesting two phosphines in mutually *cis* positions. The low-field signal is assignable to the methoxo-protons *trans* to PPh_3 since its broadness may be ascribed to coupling with two *trans*-phosphorus atoms. A single broad signal for the methoxo-protons of (IV) indicates a *trans* structure. The i.r. spectra of the methoxo-complexes showed the very strong ν(C–O) band in the expected region (1 047—1 070 cm^{-1}).

TABLE 2

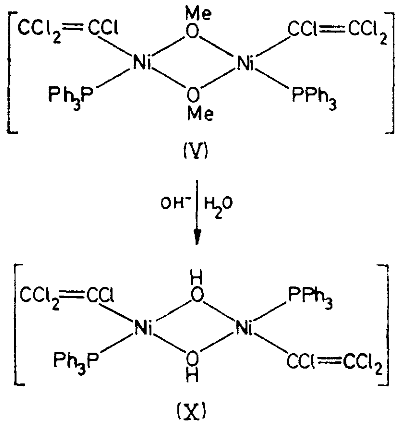
Spectral data for the methoxo-complexes

Complex	^{1}H N.m.r.[a]				I.r. (cm^{-1})[b]
	δ(OCH_3)	^4J(HP)	^3J(HPt)	Other	ν(C–O)
cis-[$Pt(C_6F_5)(OMe)(PPh_3)_2$] (I)	4 05 (d)	6.4	54	Ph: 7.50 (m), 6.80 (m)	1 055
cis-[$Pt(CCl{=}CCl_2)(OMe)(PPh_3)_2$] (I)	4.13 (d)	6.8	55	Ph: 7.60 (m), 6.90 (m)	1 062
trans-[$Pt(CH{=}CCl_2)(OMe)(PPh_3)_2$] (II)	2.97 (s)	0	27	Ph: 7.95 (m), 7.05 (m) CH: 4.98 (t) [^3J(HP) 1.0, ^2J(HPt) 25]	1 070
trans-[$Pd(C_6F_5)(OMe)(PPh_3)_2$] (III)	3.08 (t)	1.8		Ph: 7.90 (m), 7.00 (m)	1 060
trans-[$Pd(CCl{=}CCl_2)(OMe)(PPh_3)_2$] (III)	2 78 (t)	1.4		Ph: 8.06 (m), 7.10 (m)	1 068
[{$Ni(C_6F_5)(\mu\text{-}OMe)(PPh_3)$}$_2$] (IV)	1 81 (b)			Ph: 8.00 (m), 7.00 (m)	1 063
[{$Ni(CCl{=}CCl_2)(\mu\text{-}OMe)(PPh_3)$}$_2$] (V)	2.26 (b) 2.12 (s)			Ph: 8.20 (m), 7.10 (m)	1 068 1 047

[a] Measured in C_6D_6. d = Doublet, m = multiplet, s = singlet, t = triplet. δ In p.p.m. from $SiMe_4$, J in Hz. [b] Recorded in Nujol mull.

The methoxo-complexes of platinum and palladium are susceptible to hydrolysis, readily producing hydroxo-complexes. Complexes (I; R = $CCl{=}CCl_2$) and (II) in tetrahydrofuran (thf) at 60 °C reacted with water to produce *trans*-[$Pt(CCl{=}CCl_2)(OH)(PPh_3)_2$] and *trans*-[$Pt(CH{=}CCl_2)(OH)(PPh_3)_2$], (VI), respectively. Similarly, complex (III; R = $CCl{=}CCl_2$) was converted into *trans*-[$Pd(CCl{=}CCl_2)(OH)(PPh_3)_2$], (VII). The hydrolysis was accelerated by addition of a small amount of K[OH]. Alternatively, the hydroxo-complexes (VI) and (VII) were prepared more conveniently by treating *trans*- or *cis*-[$MR(Cl)(PPh_3)_2$] with Ag[BF_4] in acetone and subsequently adding aqueous K[OH] without isolating the cationic intermediate [$MR(OCMe_2)(PPh_3)_2$]$^+$. This method had been employed for the preparation of [PtMe(OH)(dppe)].[13] The following hydroxo-complexes were prepared by this method; *cis*-[$Pt(C_6F_5)(OH)(PPh_3)_2$], (VIII), *trans*-[$PtPh(OH)(PPh_3)_2$], (VI), [$PtMe(OH)(PPh_3)_2$], (IX), and *trans*-[$Pd(C_6F_5)(OH)(PPh_3)_2$], (VII). A similar reaction of *trans*-[$Pd(CH{=}CCl_2)(Cl)(PPh_3)_2$] did not give the expected hydroxo-complex; instead, ' $Pd(PPh_3)_2$ ' was obtained, a result indicative of the relative instability of the palladium analogue and of the stronger *trans* influence of $CH{=}CCl_2$ compared with that of $CCl{=}CCl_2$. The bridging methoxo-complex, (V), is stable toward water under similar conditions. This is rather surprising since [{$NiMe(\mu\text{-}OMe)(PMe_3)$}$_2$][17] is readily hydrolysed by water. However, hydrolysis of (V) takes place readily in the presence of a small amount of [OH]$^-$, affording [{$Ni(CCl{=}CCl_2)(\mu\text{-}OH)(PPh_3)$}$_2$], (X), as orange crystals.

The yield of the hydroxo-complexes of Pt^{II} is generally better than that for the corresponding palladium(II) complexes. The platinum complexes are colourless and soluble in benzene and CH_2Cl_2, except for (IX) which is only sparingly soluble in benzene. In contrast to (VI; R = $CCl{=}CCl_2$, $CH{=}CCl_2$, or Ph), (VII; R = $CCl{=}CCl_2$ or C_6F_5), and (VIII; R = C_6F_5) which are stable in CH_2Cl_2, the methyl derivative (IX) reacts readily with CH_2Cl_2 at room temperature producing *trans*-[$PtMe(Cl)(PPh_3)_2$]. The hydroxo-complexes are generally more stable toward heat and air than the corresponding methoxo-complexes. Complexes (VI; R = $CCl{=}CCl_2$ or $CH{=}CCl_2$) are particularly stable and can be stored in air for several days.



The *trans* configuration of hydroxo-complexes (VI) and (VII) is readily deduced from their n.m.r. spectra (Table 3) which showed triplet signals for the hydroxo-proton. Additional evidence for the configuration of (VI; R = $CCl{=}CCl_2$) was obtained from the ^{31}P n.m.r. spectrum which showed a singlet signal at δ −20.7 (p.p.m. from 85% H_3PO_4) with ^{195}Pt satellites [^1J(PPt) 3 066 Hz]. The triplet signal of the protons of $CH{=}CCl_2$

[J(HP) 1.5 Hz] in (VI; R = $CH{=}CCl_2$) is also consistent with the *trans* configuration. The OH proton signal of (VIII; R = C_6F_5) was a complex multiplet which did not appear to be a triplet. Although exact values for ^3J(HP) and ^2J(HPt) cannot be obtained, it is possible to say that the latter is smaller than 32 Hz. These features are only consistent with a *cis* structure. Indirect support for this structure is the departure from the chemical-shift and ν(OH) trends observed for the *trans* series (Table 3). The structure of (IX) could not be determined due to the extremely low solubility in benzene and instability in CH_2Cl_2. The *trans* configuration of the binuclear nickel complex (X), evident from the single OH proton signal, indicates geometrical isomerisation during hydrolysis of (V). The OH proton signal of (VII; R = $CCl{=}CCl_2$) disappeared in a few minutes after addition of D_2O, suggesting rapid exchange of the hydroxo-proton with D_2O.

TABLE 3

Spectral data for the hydroxo-complexes

	^{1}H N.m.r.[a]				ν(OH)/cm^{-1}	
Complex	δ(OH)	^3J(HP)	^2J(HPt)	Other	Nujol mull	CH_2Cl_2
cis-[$Pt(C_6F_5)(OH)(PPh_3)_2$] (VIII)	−2.14 (cm)			Ph: 7.55 (m), 7.40 (m)		3 617
trans-[$Pt(CCl{=}CCl_2)(OH)(PPh_3)_2$] (VI)	0.91 (t)	6.4	46.0	Ph: 7.50 (m), 7.20 (m)	3 595	3 608
trans-[$Pt(CH{=}CCl_2)(OH)(PPh_3)_2$] (VI)	−2.07 (t)	2.7	22.5	Ph: 7.70 (m), 7.45 (m) CH: 4.87(t) [^3J(HP) 1.5, ^2J(HPt) 24]	3 608	3 617
trans-[$PtPh(OH)(PPh_3)_2$] (VI)	−2.16 (t)	2.5	19.5	Ph: 7.55 (m), 7.35 (m)	3 613	3 619
[$PtMe(OH)(PPh_3)_2$] (IX) [b]					3 630, 3 660	
trans-[$Pd(C_6F_5)(OH)(PPh_3)_2$] (VII)	−2.49 (t)	4.0		Ph: 7.65 (m), 7.35 (m)	3 600	3 613
trans-[$Pd(CCl{=}CCl_2)(OH)(PPh_3)_2$] (VII)	−2.91 (t)	2.4		Ph: 7.80 (m), 7.43 (m)	3 603, 3 648	
[{$Ni(CCl{=}CCl_2)(OH)(PPh_3)$}$_2$] (X)	−3.62 (b)			Ph: 7.30 (m), 7.05 (m)	3 648	

[a] Recorded in CD_2Cl_2. cm = Complex multiplet and b = broad. δ in p.p.m. from $SiMe_4$, J in Hz. [b] Too insoluble for ^{1}H n.m.r. in organic solvents.

The i.r. spectra of the hydroxo-complexes (Table 3) showed ν(OH) in the region 3 595—3 660 cm^{-1}. The ν(OH) band in Nujol mulls was broad and weak, while it was sharp and of medium intensity in CH_2Cl_2 solution. The observation of two ν(OH) bands of (VII; R = $CCl{=}CCl_2$) and (IX) in Nujol mulls may be ascribed to intermolecular association of the OH group since a single band was observed in CH_2Cl_2 solution.

Nature and Reactivity of the M–OR *Bond*.—The shielding of the OH proton of *trans*-[$MR(OH)(PPh_3)_2$] (Table 3) depends on the ligand R in the *trans* position and increases in the sequence $C_6F_5 < CCl{=}CCl_2 < CH{=}CCl_2 <$ Ph, *i.e.* the order of increasing *trans* influence assessed on the basis of ν(Pt–Cl) of the corresponding *trans*-[$PtR(Cl)(PPh_3)_2$].* A high *trans* influence would render the *trans*-OH group more anionic through the inductive effect [11,22] and accordingly increase the shielding of the OH proton. The increase in anionic character of the OH ligand in these *trans* complexes reflects the decrease in ^2J(HPt) of the OH proton and the increase in ν(OH) (Table 3). Biphilic ligands with a stronger π-acceptor character, *e.g.* CO and NO, would increase the effective positive charge on the metal through d_π–d_π back bonding, and the electron density on the *trans*-OH group would decrease through σ–π interaction, increasing the covalency of the M–OH bond. This effect can be seen in the considerably lower chemical shift of the OH proton and lower ν(OH) of *trans*-[$Ir(NO)(OH)(PPh_3)_2$]$^+$ [δ 3.33 p.p.m., ν(OH) at 3 454 cm^{-1}] [6] and *trans*-[$Ir(CO)(OH)(PPh_3)_2$] [δ 1.7 p.p.m., ν(OH) at 3 580 cm^{-1}] [7] compared to those of *trans*-[$MR(OH)(PPh_3)_2$] (M = Pd or Pt). The strong shielding of the OH proton in (VII; R = $CCl{=}CCl_2$) and the high ν(OH) compared to the corresponding platinum complex (VI; R = $CCl{=}CCl_2$) clearly shows that the Pd–OH bonding is more ionic than the Pt–OH. Similarly, comparison of the spectroscopic data of the MeO ligand in complexes (III) (Table 2) suggests that the anionic character of this ligand also parallels the *trans* influence of the ligand R, as found for the hydroxo-complexes (VII; R = C_6F_5 or $CCl{=}CCl_2$).

One of the most convenient methods of preparing hydride complexes of the type [$MH(X)L_2$] is the reaction of metal halide complexes with alkoxide anion (alcoholic K[OH]) which presumably involves incipient formation of an alkoxo-complex followed by β elimination.[23] Some alkoxo-complexes, *e.g.* [$Pt(C_6H_9)(OMe)(dppe)$] [12] and [$Ir(NO)(OR)(PPh_3)_2$]$^+$ (R = Et or Pr^n),[6] as well as (I)—(III), are, however, stable enough to be isolated, indicating reluctance to undergo β elimination. The ease with which the initial products (III; R = C_6H_5 or $CH{=}CCl_2$) formed from *trans*-[$PdR(Cl)(PPh_3)_2$] and Na(OMe) undergo β elimination indicates the profound influence of the carbon ligand *trans* to the MeO ligand. Ready formation of *trans*-dihydride complexes [PtH_2L_2] [15] [L = PPr^i_3, $P(C_6H_{11})_3$, or PBu^t_2Ph] from oxidative addition of MeOH to [PtL_2] presumably involves the intermediates *trans*-[$PtH(OMe)L_2$]. A high *trans* influence is known for hydride and carbon ligands. It appears that the prompt β elimination is associated with an enhanced polarisation of the M–OR bond. Closely

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* For R = C_6F_5,[18] $CCl{=}CCl_2$,[19,20] $CH{=}CCl_2$,[19,20] and Ph,[21] ν(Pt–Cl) occurs at 312, 310, 305, and 284 cm^{-1}, respectively.

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related reactions may be *ortho*-palladation of azobenzene with $PdCl_2$ and *ortho*-platination of $PBu^t{}_2Ph$ in *trans*-$[PtCl_2(PBu^t{}_2Ph)_2]$,[24] for both of which evidence is available [15,25] to support electrophilic attack of the metal atom on the aromatic carbon.

In order to obtain insight into the nature of the M–OH bond, which should have bearing on the reactivity, reactions of the hydroxo-complexes with organic compounds containing active hydrogen atoms were studied. Reactions of the complexes [PtR(OH)(dppe)] [12,13] (R = Me or C_6H_9) with MeCOR, $MeNO_2$, and $CH_2(CO_2Me)_2$ afford the corresponding condensates, alkylmetal complexes. A mixture of complexes (VI; R = CCl=CCl_2 or CH=CCl_2) and $MeNO_2$ in benzene (80 °C, 6 h) produced σ-nitromethyl complexes, *trans*-$[PtR(CH_2NO_2)(PPh_3)_2]$, (XI; R = CCl=CCl_2 or CH=CCl_2). Qualitatively there is no difference in condensation rate between the two complexes (VI) (*cf.* condensations with PhCOMe, see below). Complex (VI; R = Ph) is more reactive than the above complexes and affords, under milder conditions (60 °C, 2 h), *trans*-$[PtPh(CH_2NO_2)(PPh_3)_2]$, (XI; R = Ph).

TABLE 4

Spectral data for the nitromethyl and phenacyl complexses

	¹H N.m.r.[a]				
Complex	δ(CH_2)	³*J*(HP)	²*J*(HPt)	Others	I.r. (cm^{-1}) [b]
trans-$[Pt(CCl{=}CCl_2)(CH_2NO_2)(PPh_3)_2]$ (XI)	4.32 (t)	6.0	71.0	Ph: 8.00 (m), 7.20 (m)	ν(NO_2): 1 503, 1 363
trans-$[Pt(CH{=}CCl_2)(CH_2NO_2)(PPh_3)_2]$ (XI)	4.32 (t)	5.8	62.5	Ph: 7.80 (m), 7.15 (m) CH: 4.90 (t) [³*J*(HP) 1.6, ²*J*(HPt) 19.0]	ν(NO_2): 1 508, 1 366
trans-$[PtPh(CH_2NO_2)(PPh_3)_2]$ (XI)	4.49 (t) [c]	8.0	88.0	Ph: 7.70 (m), 7.10 (m)	ν(NO_2): 1 495, 1 357
	5.02 (t) [c]	5.2	61.0		
trans-$[PtPh(CH_2COPh)(PPh_3)_2]$ (XII)	3.43 (t)	9.5	101.0	Ph: 7.85 (m), 7.50 (m), 7.20 (m), 7.10 (m), 6.90 (m)	ν(CO): 1 631
$[PtMe(CH_2COPh)(PPh_3)_2]$ (XIII) [d]					ν(CO): 1 629

[a] Recorded in benzene. δ In p.p.m. from $SiMe_4$, *J* in Hz. [b] Recorded in Nujol mulls. [c] The intensity ratio of the peaks at δ 4.49 and 5.02 p.p.m. is 2 : 1. [d] Too insoluble for ¹H n.m.r.

The nitromethyl complexes (XI) show ν(NO_2) in the expected region of the i.r. spectrum (Table 4). The *trans* configuration is inferred from the methylene-proton splitting (triplet). Consistent with this is the triplet resonance of the olefinic protons of (XI; R = CH=CCl_2). The formulation of complex (XI; R = Ph) seems to be justified on the basis of the elemental analysis and i.r. and n.m.r. data. However, we are unable to give a rationale for the observation of two triplet resonances for the CH_2 group (Table 4). Methyl phenyl ketone, which is less acidic than $MeNO_2$, reacted similarly with (VI; R = Ph) and (IX) in benzene, *trans*-$[PtPh(CH_2COPh)(PPh_3)_2]$, (XII), and $[PtMe(CH_2COPh)(PPh_3)_2]$, (XIII), respectively, being isolated. These products were characterised by elemental analysis and the spectral data (Table 4). The extremely low solubility of (XII; R = Me) in organic solvents prevents elucidation of its stereochemistry.

The relatively stable hydroxo-complexes having a *trans* ligand of considerable π-acceptor character, (VI; R = CCl=CCl_2 and CH=CCl_2), did not react with PhCOMe even under prolonged heating (80 °C, 8 h), the hydroxo-complex being recovered unchanged. These results indicate that the reactivity of the hydroxo-complex toward the condensation reaction increases with increasing anionic character of the OH ligand. Accordingly complex (VII; R = CCl=CCl_2) is expected to react with PhCOMe since the Pd–OH bond is more ionic than the Pt–OH bond in (VI; R = CCl=CCl_2). In the condensation of (VII; R = CCl=CCl_2) with PhCOMe (80 °C, in benzene), the expected alkyl product could not be isolated apparently due to its instability, metallic palladium being formed.

The reverse reaction, hydrolysis of a metal–alkyl bond to yield the hydroxometal complex, seems to have received little attention.[26] We have achieved the reversibility with appropriate alkylhydroxometal systems,

$$M{-}R + D_2O \rightleftharpoons M{-}OD + RD$$

as will be described separately. It is sufficient to note here that the reversible reaction presents a useful method of incorporating deuterium into active methyl or methylene groups.

EXPERIMENTAL

¹H N.m.r. spectra were recorded on a 100 MHz model JNM MH-100 spectrometer and i.r. spectra on a Hitachi–Perkin-Elmer model 225 instrument. Gas–liquid chromatography was carried out on Yanagimoto GCG-550-TFP system equipped with a hydrogen-flame detector. All reactions and physical measurements were made in a nitrogen atmosphere. The following reagents were prepared according to known methods: *trans*-$[PdR(Cl)(PPh_3)_2]$ (R = CCl=CCl_2 or CH=CCl_2 [27]); *trans*-$[PdBr(Ph)(PPh_3)_2]$; [28] *cis*-$[PtR(Cl)(PPh_3)_2]$ (R = C_6F_5 [18] or CCl=CCl_2 [19,20]); and *trans*-$[PtR(Cl)(PPh_3)_2]$ (R = CH=CCl_2,[19,20] CH=CHCl,[10,20] or Ph [21]). Analytical data and some physical properties of the complexes described below are shown in Table 1.

Preparation of Methoxo-complexes.—(a) cis-*Methoxo(pentafluorophenyl)bis(triphenylphosphine)platinum*(II), (I; R = C_6F_5). A solution of Na(OMe) (0.74 mmol) in

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methanol (1 cm^3) was added to a suspension of *cis*-$[Pt(C_6F_5)(Cl)(PPh_3)_2]$ (0.18 g, 0.2 mmol) in toluene (10 cm^3) and the mixture was stirred at 65 °C for 5 h. The mixture was filtered and after concentration *in vacuo* a pale yellow solid was obtained. Recrystallisation (n-hexane–toluene) gave colourless *crystals* (0.12 g, 80%).

(b) cis-*Methoxo(trichlorovinyl)bis(triphenylphosphine)platinum*(II), (I; R = $CCl{=}CCl_2$). The complex was prepared as in (a), using Na(OMe) (1.8 mmol) and *cis*-$[Pt(CCl{=}CCl_2)(Cl)(PPh_3)_2]$ (0.18 g, 0.2 mmol) as colourless *crystals* (0.10 g, 60%).

(c) trans-(2,2-*Dichlorovinyl)methoxobis(triphenylphosphine)platinum*(II), (II; R = $CH{=}CCl_2$). A similar reaction using Na(OMe) (1.5 mmol) and *trans*-$[Pt(CH{=}CCl_2)(Cl)(PPh_3)_2]$ (0.34 g, 0.4 mmol) gave colourless *crystals* (0.12 g, 80%).

(d) trans-*Methoxo(pentafluorophenyl)bis(triphenylphosphine)palladium*(II), (III; R = C_6F_5). A solution of Na(OMe) (0.5 mmol) in methanol (1 cm^3) was added to a solution of *trans*-$[Pd(C_6F_5)(Cl)(PPh_3)_2]$ (0.24 g, 0.29 mmol) in toluene (5 cm^3). After stirring at 40 °C for 2.5 h, the yellow solution was filtered. The concentrated residue was recrystallised from n-hexane–toluene as pale yellow *crystals* (0.12 g, 50%).

(e) trans-*Methoxo(trichlorovinyl)bis(triphenylphosphine)palladium*(II), (III; R = $CCl{=}CCl_2$). A similar reaction using Na(OMe) (0.64 mmol) and *trans*-$[Pd(CCl{=}CCl_2)(Cl)(PPh_3)_2]$ (0.15 g, 0.17 mmol) gave pale yellow *crystals* (0.12 g, 80%). These were contaminated with a trace amount of colourless crystals, $\nu_{max.}$ (in Nujol) at 1 866 cm^{-1} [ν(Pd–H)]. A pure sample of (III) was obtained after several recrystallisations from toluene–n-hexane.

(f) *Bis[μ-methoxo-(pentafluorophenyl)(triphenylphosphine)nickel*(II)], (IV). A solution of Na(OMe) (0.8 mmol) in methanol (1 cm^3) was added to a suspension of $[Ni(C_6F_5)(Cl)(PPh_3)_2]$ (0.18 g, 0.23 mmol) in toluene (3 cm^3). The mixture was stirred at ambient temperature for 0.5 h to give a clear dark red solution. Filtration and subsequent concentration of the filtrate gave a dark red oil, which crystallised on addition of n-hexane. Recrystallisation from n-hexane gave red *crystals* (0.05 g, 45%).

(g) *Bis[μ-methoxo-(trichlorovinyl)(triphenylphosphine)nickel*(II)], (V). A similar reaction using Na(OMe) (0.55 mmol) and $[Ni(CCl{=}CCl_2)(Cl)(PPh_3)_2]$ (0.30 g, 0.4 mmol) gave red *crystals* (0.17 g, 90%).

Reaction of trans-*Chloro*(2,2-*dichlorovinyl)bis(triphenylphosphine)palladium*(II) *with* Na(OMe).—A suspension of *trans*-$[Pd(CH{=}CCl_2)(Cl)(PPh_3)_2]$ (0.24 g, 0.3 mmol) in toluene (3 cm^3) was treated with a solution of Na(OMe) (0.5 mmol) in methanol (1 cm^3) at 40 °C for 4 h. The mixture was distilled *in vacuo* (15 mmHg) * at room temperature. V.p.c. analysis (P.E.G. 20m, 80 °C) of the distillate showed the presence of HCHO and $CH_2{=}CCl_2$. The solid residue was recrystallised from toluene–n-hexane to give very air-sensitive yellow crystals which did not contain chlorine. Treatment of the yellow crystals with PPh_3 (0.156 g, 0.6 mmol) in toluene (5 cm^3) gave $[Pd(PPh_3)_4]$ (0.10 g, 30%).

Reaction of trans-*Bromo(phenyl)bis(triphenylphosphine palladium*(II) *with* Na(OMe).—A solution of *trans*-$[PdBr(Ph)(PPh_3)_2]$ (0.31 g, 0.4 mmol) in toluene (3 cm^3) was treated with Na(OMe) (0.88 mmol) in MeOH (0.5 cm^3) at 50 °C for 3 h. V.p.c. analysis of the distillate from the reaction mixture showed benzene (80%), HCHO (*ca.* 20%), and anisole (trace).

Preparation of Hydroxo-complexes.—(a) trans-*Hydroxo(trichlorovinyl)bis(triphenylphosphine)platinum*(II), (VI; R = $CCl{=}CCl_2$). *Method* (A). A mixture of (I; R = $CCl{=}CCl_2$) (0.09 g, 0.1 mmol) and 10^{-5}N aqueous NaOH (0.5 cm^3) in thf (5 cm^3) was stirred at 60 °C for 6 h. After evaporation to dryness, the solid residue was recrystallised from tetrahydrofuran–n-hexane as colourless *crystals* (0.05 g, 60%). Hydrolysis of (I) took place even in the absence of NaOH (70 °C, 6 h).

Method (B). A mixture of *cis*-$[Pt(CCl{=}CCl_2)(Cl)(PPh_3)_2]$ (0.26 g, 0.3 mmol) and $Ag[BF_4]$ (0.06 g, 0.3 mmol) in acetone (10 cm^3) was stirred at room temperature for 3 h. After filtration of AgCl, a solution of K[OH] (0.02 g, 0.36 mmol) in water (1 cm^3) was added to the filtrate with vigorous stirring. After 2 h at room temperature, the solvent was removed under reduced pressure and the residue was extracted with benzene. Concentration of the extract and subsequent addition of n-hexane gave (VI) (0.15 g, 60%).

(b) trans-(2,2-*Dichlorovinyl)hydroxobis(triphenylphosphine)platinum*(II), (VI; R = $CH{=}CCl_2$). The complex was prepared from (II; R = $CH{=}CCl_2$) (0.09 g, 0.1 mmol) by method (A) as colourless *crystals* (0.03 g, 40%), and also from *trans*-$[Pt(CH{=}CCl_2)(Cl)(PPh_3)_2]$ (0.26 g, 0.3 mmol) by method (B) (0.15 g, 60%).

(c) trans-*Hydroxo(trichlorovinyl)bis(triphenylphosphine)palladium*(II), (VII; R = $CCl{=}CCl_2$). A mixture of (III; R = $CCl{=}CCl_2$) (0.27 g, 0.35 mmol) and 10^{-5}N aqueous NaOH in thf (15 cm^3) was stirred at 40 °C for 4 h. The solvent was removed under reduced pressure, and the residue was recrystallised from n-hexane–toluene as colourless *crystals* (0.12 g, 45%). The complex was also prepared from *trans*-$[Pd(CCl{=}CCl_2)(Cl)(PPh_3)_2]$ (0.16 g, 0.2 mmol) by method (B) (0.05 g, 30%).

(d) *Hydroxo(pentafluorophenyl)bis(triphenylphosphine)platinum*(II), (VIII). This was prepared from *cis*-$[Pt(C_6F_5)(Cl)(PPh_3)_2]$ (0.42 g, 0.5 mmol) by method (B) as colourless *crystals* (0.12 g, 30%).

(e) trans-*Hydroxo(phenyl)bis(triphenylphosphine)platinum*(II), (VI; R = Ph). The complex was prepared from *trans*-$[PtPh(Cl)(PPh_3)_2]$ (0.16 g, 0.2 mmol) by method (B) as colourless *crystals* (0.12 g, 70%).

(f) trans-*Hydroxo(methyl)bis(triphenylphosphine)platinum*(II), (IX). The complex was prepared from *trans*-$[PtMe(I)(PPh_3)_2]$ (0.19 g, 0.2 mmol) by method (B) as colourless crystals (0.10 g, 70%).

(g) trans-*Hydroxo(pentafluorophenyl)bis(triphenylphosphine)palladium*(II), (VII; R = C_6F_5). The complex was prepared from *trans*-$[Pd(C_6F_5)(Cl)(PPh_3)_2]$ (0.16 g, 0.2 mmol) by method (B) as colourless crystals (0.05 g, 30%).

(h) *Bis[μ-hydroxo-(trichlorovinyl)(triphenylphosphine)nickel*(II)], (X). A mixture of (V) (0.19 g, 0.2 mmol) and 10^{-5}N aqueous NaOH in thf was stirred at room temperature for 1 h. After evaporation to dryness, the solid residue was recrystallised from n-hexane–toluene as orange *crystals* (0.02 g, 10%). Hydrolysis of (V) took place even in the absence of NaOH, but required prolonged stirring (15 h).

Reaction of Hydroxo-complexes.—*With* $MeNO_2$. (a) trans-(*Nitromethyl)(trichlorovinyl)bis(triphenylphosphine)platinum*(II), (XI; R = $CCl{=}CCl_2$). A mixture of (VI; R = $CCl{=}CCl_2$) (0.20 g, 0.24 mmol) and $MeNO_2$ (1 cm^3, 18 mmol) in benzene (5 cm^3) was stirred at 80 °C for 6 h. After

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

filtration and subsequent concentration, n-hexane was added to give colourless crystals (0.12 g, 50%).

(b) trans-*(2,2-Dichlorovinyl)(nitromethyl)bis(triphenylphosphine)platinum*(II), (XI; R = $CH{=}CCl_2$). This was prepared as in (a) from (VI; R = $CH{=}CCl_2$) (0.05 g, 0.06 mmol) as colourless *crystals* (0.03 g, 60%).

(c) trans-*(Nitromethyl)(phenyl)bis(triphenylphosphine)platinum*(II), (XI; R = Ph). This was prepared as in (a) from (VI; R = Ph) (0.03 g, 0.04 mmol), but under mild conditions (60 °C, 2 h), as colourless *crystals* (0.02 g, 70%).

With PhCOMe. (a) trans-*Phenacyl(phenyl)bis(triphenylphosphine)platinum*(II), (XII). A mixture of (VI; R = Ph) (0.035 g, 0.04 mmol) and PhCOMe (0.5 cm^3, 4.5 mmol) was heated at 80° for 3 h. After filtration and subsequent concentration of the filtrate *in vacuo*, n-hexane was added to give colourless crystals (0.02 g, 60%).

(b) *Methyl(phenacyl)bis(triphenylphosphine)platinum*(II), (XIII). A mixture of (IX) (0.15 g, 0.2 mmol) and PhCOMe (0.5 cm^3, 4.5 mmol) in benzene was heated at 60 °C for 4 h. Colourless *crystals* separated and were filtered off, washed with benzene, and dried *in vacuo* (0.08 g, 50%).

The other hydroxo-complexes of Pt^{II}, (VI; R = $CH{=}CCl_2$ and $CCl{=}CCl_2$), did not react with PhCOMe at 80 °C for 8 h.

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