64. *Tertiary Phosphine Complexes of Trimethylgold: Infrared Spectra of Complexes of Gold and Some Other Metals.*

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Trimethyl- and triphenyl-phosphine displace ethylenediamine from its bis(trimethylgold) complex. Thermal decomposition of PPh_3AuMe_3 gives ethane, the gold(I) complex, and finally the tertiary phosphine and gold. Its dipole moment (5·2 D) is a little less than that of PPh_3AuMe (5·6 D), indicating more P–Au back-donation.

Gold–phosphorus infrared stretching frequencies of several trimethylphosphine complexes fall in the range 347—391 cm.$^{-1}$. Metal–phosphorus stretching frequencies of halides $(PMe_3)_2MX_2$, (M = Ni, Pd, or Pt; X = Cl, Br, or I) fall within an even narrower range, and the absence of trend with atomic weight of the metal indicates increased π-bonding with increase of atomic weight in this series. Gold–chlorine and –bromine frequencies (311—329 and 210—233 cm.$^{-1}$) for some gold(I) complexes are reported and are compared with the higher frequencies of gold(III) complexes. Metal-chlorine stretching frequencies in *trans*-complexes are in the ranges 404—408 (Ni), 353—359 (Pd), and 326—339 cm.$^{-1}$ [Pt(II)]. For *cis*-complexes ν(M–Cl) is lower, covers a wider range, and is affected more by the other ligands. Both $(PMe_3)_2PdCl_2$ and $(AsMe_3)_2PdCl_2$ have *cis*-structures in the solid state.

TRIMETHYLGOLD(III) complexes with some amines have been prepared by the addition of amines to the very unstable solution of trimethylgold(III) in diethyl ether prepared by addition of methyl-lithium to a suspension of gold(III) bromide at low temperatures.[1]

[1] Gilman and Woods, *J. Amer. Chem. Soc.*, 1948, **70**, 550.

Though amine complexes of methylgold(I) have not yet been described, a series of complexes between phenylethynylgold(I) and a variety of donor molecules has been examined, and tertiary phosphines have been shown to displace amines,[2] *e.g.*, $Ph \cdot C \vdots C \cdot AuNH_2Pr^i$ + $PPh_3 \longrightarrow Ph \cdot C \vdots C \cdot AuPPh_3 + Pr^i \cdot NH_2$.

We find that ethylenediamine is displaced from its bistrimethylgold(III) complex by trimethyl- or triphenyl-phosphine. The complex Me_3AuPMe_3, m. p. 23°, is sufficiently volatile to be sublimed at low pressure at room temperature. The tertiary phosphine complexes may also be obtained by direct addition of tertiary phosphine to ethereal trimethylgold at about −70°.

Some methylplatinum(II) complexes have been converted into dimethylplatinum(IV) complexes by direct addition of methyl iodide;[3] in the course of this study Chatt and Shaw found that thermal decomposition of bistriethylphosphinedi-iodo(dimethyl)platinum(IV) at 80°/0·01 mm. yielded *trans*-bistriethylphosphineiodo(methyl)platinum(II) and, presumably, methyl iodide. However, they reported that prolonged heating (20 hours at 100°) in a sealed tube gave ethane: $(PEt_3)_2PtMe_2I_2 \longrightarrow (PEt_3)_2PtI_2 + C_2H_6$. As the much less stable methyl derivatives of palladium decompose in a complicated way suggestive of a free-radical decomposition,[4] we have examined the effect of heating trimethyl-(triphenylphosphine)gold(III). In a series of experiments in which the gold(III) complex was heated alone, in xylene, and in biphenyl, ethane was the only volatile decomposition product detected:

$$PPh_3AuMe_3 \longrightarrow C_2H_6 \ (87\%) + PPh_3AuMe \longrightarrow C_2H_6 \ (95\%) + PPh_3 + Au$$
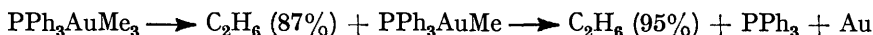
These reactions took place in vessels attached to a vacuum apparatus for the quantitative manipulation of gases, and methane would have been detected had it been present. Decomposition of the gold(III) compound in xylene at 120° gave ethane equivalent to only 57% of the methyl groups present, but no methane was detected; methyl(triphenyl-phosphine)gold(I) was identified after removal of the xylene. Similarly, decomposition of the methylgold(I) complex in biphenyl at 175° gave gold, triphenylphosphine, and ethane corresponding to only 48% of the methyl, and no methane.

Though it is possible that the trimethylgold(III) complex could re-arrange to a monomethylgold(I) complex and ethane without the intermediate formation of methyl radicals, it is difficult to see how the decomposition of the monomethylgold(I) complex could proceed without the transient formation of methyl radicals. The absence of methane from the decomposition products indicates that methyl radicals, if formed, do not react by hydrogen abstraction but rather by abstraction of a methyl group from another PPh_3AuMe molecule, and perhaps by addition to solvent or phosphine molecules.

The dipole moments of some alkylgold(I) tertiary phosphine complexes [2,5] are in the range 5·4—5·6 D, the methyl compound PPh_3AuMe having a moment of 5·6 D (benzene solution). The dipole moment of the corresponding trimethylgold complex, PPh_3AuMe_3, is 5·2 D. This difference indicates a rather higher degree of back-donation (d_π–d_π bonding) in the Au–P bond in the Au(III) complex. It is worth mentioning that, of all the organo-gold compounds we have handled, trimethyl(triphenylphosphine)gold(III) showed the least tendency to decompose with formation of metallic gold. Also the highest of all the ν(Au–PMe_3) infrared frequencies measured was that of the gold(III) complex PMe_3AuMe_3 (see below).

We consider that the lower moment of the trimethylgold(III) complex is due to the inductive effect of the methyl groups, rather than to a change in the valency state of the gold. The dipole moments of PEt_3AuX_3 (X = Cl, 9·6$_2$; Br, 9·5$_0$; I, 8·6$_9$ D) are considerably greater than those of the corresponding gold(I) compounds PEt_3AuX (X = Cl, 8·3$_8$; Br, 8·3$_5$; I, 8·3$_5$ D), again, we consider, owing to inductive effects.

[2] Coates and Parkin, *J.*, 1962, 3220.
[3] Chatt and Shaw, *J.*, 1959, 705, 4020.
[4] Calvin and Coates, *J.*, 1960, 2008.
[5] Calvin, Coates, and Dixon, *Chem. and Ind.*, 1959, 1628.

Infrared Spectra.—Gold–methyl stretching. Methylgold(I) complexes with tertiary phosphines [5] have a single band near 530 cm.$^{-1}$, but two bands were observed in the spectra of the trimethylgold(III) complexes corresponding to symmetrical and unsymmetrical stretching. The ethylenediamine complex, $(Me_3Au)_2$en, has two bands, at 504 and 477 cm.$^{-1}$, the former being the more intense, clearly owing to AuC_3 unsymmetrical and symmetrical stretching vibrations, respectively. In the trimethylphosphine complex, Me_3AuPMe_3, these bands are shifted to higher frequencies, 541 and 498, suggesting that the gold–carbon bonds are stronger. The spectrum of the triphenylphosphine complex is more complex in the 450—550 cm.$^{-1}$ region, on account of phosphine bands at 544 and 488, corresponding to the 541 and 494 cm.$^{-1}$ bands of PPh_3AuCl, but the AuC_3 bands at 530 and 512 cm.$^{-1}$ are quite evident and are the same when the sample is pressed in a potassium bromide disc as when the spectrum is measured for a benzene solution. The lower AuC_3 stretching frequencies of the amine complex, suggestive of weaker bonding, agree with the fact that, unlike the phosphine complexes, the amine complex explodes when heated.

Bands due to the symmetrical deformation $\delta_{Me(s)}$ of methyl groups bound to platinum(II) are in the range 1170—1230 cm.$^{-1}$ and vary greatly in intensity.[6] For PMe_3AuMe_3, $\delta_{Me(s)}$ bands of medium intensity are at 1177, 1190, and 1209 cm.$^{-1}$ (liquid film), no bands being present in the spectrum of PMe_3AuCl in this region. However, in the spectrum of PMe_3AuMe the only bands in this region, at 1159 and 1170 cm.$^{-1}$, are so faint as to be barely discernible. The spectra of triphenylphosphine complexes are congested in this region, and $\delta_{Me(s)}$ cannot be identified for methyl(triphenylphosphine)gold complexes with any certainty. In spectra of the sulphur complexes, Me_2AuSMe and Me_2AuSPh, $\delta_{Me(s)}$ bands are relatively intense, at 1183, 1208, and 1186, 1212 cm.$^{-1}$ respectively (KBr discs).

Gold–phosphorus and gold–halogen stretching. In the long-wavelength region (20—50 μ) methyl(trimethylphosphine)gold(I) has a single band of moderate intensity at 357 cm.$^{-1}$ (pressed in a cæsium iodide disc), and PMe_3AuMe_3 (liquid film) has a rather weak and broad band at 391 cm.$^{-1}$. These bands are assigned to the gold–phosphorus stretching vibration on the basis of a comparison with the spectra of a series of other tertiary phosphine complexes. For example, PMe_3AuCl has a sharp band at 381 cm.$^{-1}$ which we consider due to Au–P stretching, a strong band at 311 cm.$^{-1}$ with a shoulder at 305 cm.$^{-1}$, clearly due to $\nu(Au-^{35}Cl)$ and $\nu(Au-^{37}Cl)$, and a very weak band at 273 cm.$^{-1}$ which is in the region where $P(CH_3)_3$ bending vibrations occur (*e.g.*, 256 cm.$^{-1}$ in Me_3PO,[7] 302 cm.$^{-1}$ in Me_3PCl_2 and Me_3PBr_2 [8]). Stretching frequencies of bonds between phosphorus and heavier elements have already been reported,[8] *e.g.*, $\nu(P-Br)$ is 415 cm.$^{-1}$ in $[Me_3P-Br]Br$ and $\nu(P-I)$ is 358 cm.$^{-1}$ in $[Me_3P-I]I$. Isotopic splitting is clearer for compounds containing one Au–Cl bond than for those containing more than one chlorine bound to the same gold atom; for example, the unsymmetric stretching vibration in the $AuCl_2^-$ anion would be expected to be split into three, $^{37}Cl^{35}Cl$, $^{37}Cl^{37}Cl$, and $^{35}Cl^{35}Cl$. The fact that there is only one stable isotope of gold helps to make Au–Cl isotopic splitting clearer than in the case of chlorides of elements consisting of a mixture of stable isotopes.

Gold–phosphorus bands are much stronger in complexes of trimethylphosphine than of other tertiary phosphines. The very weak band at 388 cm.$^{-1}$ (PEt_3AuMe) is almost certainly due to an Au–P vibration, but in chloro(triphenylphosphine)gold(I) (Figure), which shows the Au–Cl isotopic splitting (6 cm.$^{-1}$) particularly well, the weak band at 444 cm.$^{-1}$ is a vibration of the triphenylphosphine group since many di- and tri-phenyl-phosphine compounds have bands in this region.

Infrared data, mainly on gold(I) complexes, are summarised in Table 1. The trimethylphosphine complexes (IV), (V), (VI), (IX), and (XII) have medium-to-weak bands at 303, 288, 273, 271, and 269 cm.$^{-1}$ which are all probably due to a PC_3 bending vibration

[6] Adams, Chatt, and Shaw, *J.*, 1960, 2047.
[7] Goubeau and Berger, *Z. anorg. Chem.*, 1960, **304**, 147.
[8] Goubeau and Baumgärtner, *Z. Elektrochem.*, 1960, **64**, 598.

(as mentioned above in the case of VI). Similarly a weak band at 278 cm.$^{-1}$ for (XIII) could be due to SC$_2$ bending. The spectra of the complexes listed in Table 1 are relatively simple in the 22—50 μ region and, apart from bands at 444 (VIII) and 441 cm.$^{-1}$ (XI) due to a phenylphosphine vibration, all observed bands may be assigned.

Wavelength (mμ)
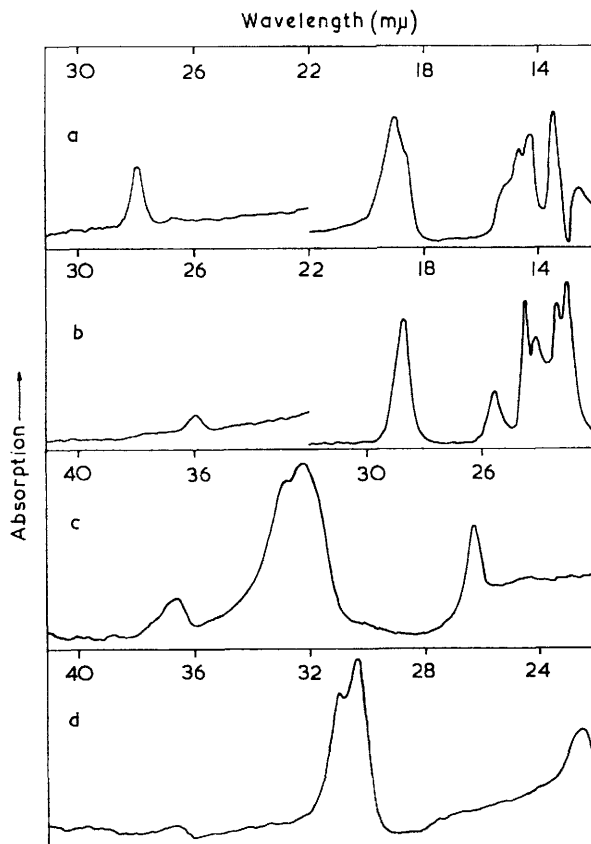
Infrared spectra of (a) Me$_3$PAuMe, (b) Et$_3$PAuMe, (c) Me$_3$PAuCl, and (d) Ph$_3$PAuCl.

The observed gold–phosphorus stretching frequencies lie in the range 347—391 cm.$^{-1}$. Apart from the regular change in the series PMe$_3$AuX (X = Cl, Br, I), no regularities are found. In particular it is remarkable that the Au–P frequency in PMe$_3$AuMe is less than in the halide complexes.

The range of gold–chlorine frequencies is smaller, 311—329 cm.$^{-1}$ (referring to the

TABLE 1.

Infrared stretching frequencies (cm.$^{-1}$) of gold complexes.

	Complex	ν(Au–P)	ν(Au–X)		Complex	ν(Au–P)	ν(Au–X)
I	PMe$_3$AuMe *	357m		X	PEt$_3$AuBr	—	210s
II	PEt$_3$AuMe	388vw		XI	PPh$_3$AuBr	—	233s, 229sh
III	PMe$_3$AuMe$_3$ †	391w (broad)		XII	PMe$_3$AuI	371s	— ¶
IV	PMe$_3$AuC⦂CBu^t	368m		XIII	SMe$_2$AuCl	344s ‡	324·5s, 319·5sh
V	PMe$_3$AuC⦂CPh	347s		XIV	SMe$_2$AuBr	absent	228m
VI	PMe$_3$AuCl	381m	311s, 305sh	XV	AsMe$_3$AuCl	265s §	317s, 312s
VII	PEt$_3$AuCl	—	312s, 305sh	XVI	AsMe$_3$AuBr	absent	210s
VIII	PPh$_3$AuCl	—	329s, 323ms	XVII	AsMe$_3$AuI	268s §	— ¶
IX	PMe$_3$AuBr	376s	226s				

* CsI disc. † Liquid film. ‡ ν(Au–S). § ν(Au–As). ¶ Beyond 50 μ.

[35]Cl component) than that of the gold–bromine frequencies, 210—233 cm.[-1]. Though ν(Au–Cl) in the series SMe_2AuCl, $AsMe_3AuCl$, PMe_3AuCl decreases as the π-bonding character of the donor atom increases, no such regularity is found among the bromides.

The low-frequency spectra of some gold(III) halide complexes are summarised in Table 2. The Raman spectra of aqueous solutions of $KAuCl_4$ and $KAuBr_4$ have already been studied,[9] and the symmetrical A_{1g} and out-of-phase B_{2g} stretching frequencies (infrared inactive) are at 347, 324, and 212, 196 cm.[-1], respectively. The infrared bands now reported, due to the E_u unsymmetric vibration, are at higher frequencies, as expected. Bending modes are below 200 cm.[-1] in the Raman spectra, and infrared-active bending modes would be beyond the range of our present instrument. The black cæsium complexes (XXVII and XXVIII) contain $AuCl_4$ anions, and their absorptions at 350 and 354 evidently correspond to the 356 cm.[-1] band of $CsAuCl_4$. The lower-frequency band at 340 cm.[-1] in the spectrum of (XXVII) must be due to ν(Au–Cl) in the $AuCl_2$ anion. The spectrum of (XXVIII) is perplexing in respect of the absence of any band that could be due to ν(Ag–Cl), other than a possible coincidence with ν(Au–Cl) at 354 cm.[-1].

The other complexes listed in Table 2 have lower symmetry and more than one Au–X stretching frequency should be observed. The two pyridine complexes each have two

TABLE 2.

Infrared spectra of gold(III) halide complexes.

	Complex	ν(Au–Cl)	ν(Au–Br)	Other bands
XVIII	$CsAuCl_4$	356s	—	—
XIX	$KAuBr_4$	—	249s	—
XX	$pyAuCl_3$	365s, 357sh	—	334vw
XXI	$pyAuBr_3$	—	264sh, 261s	227vw
XXII	PMe_3AuBr_3	—	260s, 213s	366w, 300w
XXIII	PEt_3AuCl_3	370s, 301s, 296sh	—	421w, 397vw, 347vw
XXIV	PEt_3AuCl_2Br	371s, 302s, 296sh	—	423m, 344vw
XXV	$PEt_3AuClBr_2$	311s, 305sh	263m	422m, 377vw 366w, 348m
XXVI	PEt_3AuBr_3	—	263s, 215s	421m, 376w 330vw, 241vw
XXVII	$Cs_2Au_2Cl_6$	350s, 340s	—	—
XXVIII	$Cs_2AgAuCl_6$	354s	—	272w, broad

strong bands close together, but in contrast the tertiary phosphine complexes have two or more rather widely spaced bands. For example, the tribromides (XXII) and (XXVI) have strong bands at 260, 213, and 263, 215 cm.[-1], respectively, which could be associated with valency vibrations perpendicular and parallel to the P–Au–Br axis. No band that could be associated with ν(Au–Br) was observed in the spectrum of (XXIV), possibly because it may be lower than 200 cm.[-1].

Several bands are found in the 340—400 cm.[-1] region, and in only one instance (XXII) is it possible to assign ν(Au–P) with any confidence (366 cm.[-1]). All four triethylphosphine complexes have a band in the range 421—423 cm.[-1].

Comparison with nickel, palladium, and platinum complexes. Largely to obtain data in support of our analysis of the spectra of gold complexes, we have examined some complexes (mainly tertiary phosphine) of nickel, palladium, and platinum halides. As spectroscopic techniques improve, results have recently been obtained for various heavy-metal–halogen stretching frequencies, but we have not been able to find data on stretching frequencies of metal–phosphorus, –arsenic, or –sulphur bonds in complexes containing phosphines, arsines, or sulphides.

The following data indicate that heavy metal–chlorine and –bromine stretching frequencies are likely to be in the range 200—400 cm.[-1]: ν unsym ($HgCl_2$, gas) 413, ($HgBr_2$,

[9] Stammreich and Forneris, *Spectrochim. Acta*, 1960, **16**, 363.

gas) 293; [10] ν(Sn–Cl) ($Bu^n_2SnCl_2$, 348 and 332 [11]), (Me_3SnCl, 315 [12]); ν unsym (M–Cl) (M = Zr, 422; Hf, 393; Th, 335; [13] Ti, 485; V, 475; [14] Cr, in CrO_2Cl_2, 475, 499 [15]); ν(Ti–Br) in $TiBr_4$, 230 (sym), 383 (unsym); [16] ν(V–Br) in $VOBr_3$, 271 (sym), 400 (unsym); ν(As–Br) in $AsBr_3$, 285 (sym), 275 (unsym).[17]

Metal–chlorine infrared-active stretching frequencies in some complex halides of rhenium, palladium, osmium, iridium, and platinum lie in the range [18] 313—358 cm.$^{-1}$,

TABLE 3.

Infrared spectra of nickel, palladium, and platinum(II) complexes, L_2MX_2.

Complex	ν(M–L)	ν(M–X)	Other bands
$(PMe_3)_2NiCl_2$	361w	403s	276m, 250m
$(PPhMe_2)_2NiCl_2$	342·5m(?)	404s	417w, 324m, 247m
$(PPhEt_2)_2NiCl_2$	345m(?)	408s	380w, 317m, 293w
			255w
$(PMe_3)_2NiBr_2$	360w	340m	268m, 249m
$(PMe_3)_2NiI_2$	366s	280m	251m
$(Me_2NCH_2^-)_2PdCl_2$	—	330s, 321·5s	248w, 242m
$(Me_2NC_2H_4NH_2)PdCl_2$	—	331sh, 321s	
$(Me_2NC_3H_4NHMe)PdCl_2$	—	331s, 321s	
$C_2H_4(NH_2)_2PdCl_2$	—	306s, 272m	342·5w
$trans$-$(NH_3)_2PdCl_2$	—	332s	224s, broad
$trans$-py_2PdCl_2	—	356s	277w, 267m, 228vw
cis-$(PMe_3)_2PdCl_2$	365w	294sh, 283s, 269s	251w, 231s
$(PMe_3)_2PdBr_2$	344w	—	270sh, 261w, 251w
$(PMe_3)_2PdI_2$	341m	—	284m
cis-$(PMe_3)_2PdMe_2$	365w, 347w	—	379vw
$trans$-$(PEt_3)_2PdCl_2$	409w	355s	328w
$trans$-$(PPr_3^n)_2PdCl_2$	420vw	353s	
$trans$-$(PBu_3^n)_2PdCl_2$	—	355m	
$trans$-$(PPh_3)_2PdCl_2$	—	357s	438w
$(Ph_2PCH_2^-)_2PdCl_2$	389w(?)	310s, 286s	429vw
$trans$-$(PEt_3)_2PdBr_2$	408m, or 376w	—	329w
$trans$-$(PEt_3)_2PdI_2$	408m, or 380w	—	332vw
cis-$(AsMe_3)_2PdCl_2$	258s, 251s, 242s	316s, 298·5s	
$(AsMe_3)_2PdBr_2$	276m	—	
$(AsMe_3)_2PdI_2$	269m	—	
$trans$-$(AsEt_3)_2PdCl_2$	—	353s	328w, 303w
$trans$-$(SMe_2)_2PdCl_2$	—	359s	309m, 292m
$trans$-$(SEt_2)_2PdCl_2$	—	358s	300m
$(MeS·CH_2^-)_2PdCl_2$	338·5s	314·5s, 296s	241m, 214m
$(EtS·CH_2^-)_2PdCl_2$	—	322·6m, 309·6w	
Cyclo-octa-1,5-diene $PdCl_2$	—	335s, 325s, 296s	
cis-$(PMe_3)_2PtCl_2$	377m, 362m	302m, 288m, 277m	
$trans$-$(PMe_3)_2PtCl_2$	364w	326vs	
cis-$(PEt_3)_2PtCl_2$	372w	305s, 283s	
$trans$-$(PEt_3)_2PtCl_2$	413w, or 382w	339s	
cis-$(PEt_3)_2PtBr_2$	379w	—	331vw
cis-$(AsMe_3)_2PtCl_3$	267s	312·5s, 293s	
$trans$-$(AsMe_3)_2PtCl_2$	265vw(?)	337m	

and indicate that in the case of platinum ν(Pt–Cl) is higher for platinum(IV) than for platinum(II).

The spectra of some nickel, palladium, and platinum(II) complexes in the 22—50 μ region are summarised in Table 3.

Metal–phosphorus stretching frequencies are mostly in the range 340—400 cm.$^{-1}$, but assignments are uncertain except in the case of trimethylphosphine complexes which

[10] Klemperer and Lindeman, *J. Chem. Phys.*, 1956, **25**, 397.
[11] Tobin, *J. Mol. Spectroscopy*, 1960, **5**, 65.
[12] Kriegsmann and Pischtschan, *Z. anorg. Chem.*, 1961, **308**, 212.
[13] Büchler, Berkowitz-Mattuck, and Dugre, *J. Chem. Phys.*, 1961, **34**, 2202.
[14] Dove, Creighton, and Woodward, *Spectrochim. Acta*, 1962, **18**, 267.
[15] Hobbs, *J. Chem. Phys.*, 1958, **28**, 1220.
[16] Miller and Carlson, *Spectrochim. Acta*, 1960, **16**, 6.
[17] Miller and Baer, *Spectrochim. Acta*, 1961, **17**, 112.
[18] Adams, *Proc. Chem. Soc.*, 1961, 335.

are in a narrower range 341—377 cm.$^{-1}$. Since there is little variation between corresponding complexes of the three metals [*e.g.*, 361 in $(PMe_3)_2NiCl_2$ and 364 in *trans-*$(PMe_3)_2PtCl_2$], the metal–phosphorus force constant must increase with atomic weight of the metal in agreement with current views about the extent of metal–phosphorus d_π-bonding. Thus the effect of increasing the atomic weight of the metal must be compensated by a corresponding increase in metal–phosphorus π-bonding. The gold(I)–PMe_3 frequencies are nearly all in the same range, *viz.*, 347—381 cm.$^{-1}$. Palladium–arsenic (242—276) and platinum–arsenic (265 and 267) frequencies are also about the same as the two gold–trimethylarsine frequencies observed (Table 1, 265 and 268 cm.$^{-1}$).

In contrast, the metal–chlorine frequencies vary considerably over the series Ni, Pd, Pt, Au. In the *trans-*complexes of nickel, palladium, and platinum only one metal–chlorine vibration would be infrared-active, and $\nu(M-Cl)$ is in the range 403—408 cm.$^{-1}$ (nickel), 353—359 cm.$^{-1}$ (palladium, irrespective of the donor molecule, except for the diammine), and 326—339 cm.$^{-1}$ [platinum(II)].

Bands due to metal–bromine stretching were not observed for the two palladium and one platinum compounds studied; they may be outside the range of the spectrometer, though Au–Br frequencies (210—233 cm.$^{-1}$, Table 1) were observed for gold(I) complexes. The band at 340 cm.$^{-1}$ in the spectrum of $(PMe_3)_2NiBr_2$ is assigned to $\nu(Ni-Br)$ by analogy with the unsymmetric stretching frequencies of other first-row transition metals (Ti, 383 cm.$^{-1}$ in $TiBr_4$;[16] and V, 400 cm.$^{-1}$ in $VOBr_3$[17]). The band at 280 cm.$^{-1}$ in the spectrum of $(PMe_3)_2NiI_2$ is assigned to $\nu(Ni-I)$ rather than the 251 cm.$^{-1}$ band, since a band near 250 cm.$^{-1}$ is found in very many trimethylphosphine complexes and is almost certainly due to a PC_3 bending vibration. Also, the band at 280 cm.$^{-1}$ is sharper than that at 251 cm.$^{-1}$, and we find that metal–halogen bands are generally relatively sharp, whereas the 250 cm.$^{-1}$ band for trimethylphosphine complexes is broad.

Complexes of *cis-*configuration would be expected to have two M–L and two M–X infrared active stretching frequencies. Though two, and sometimes three, bands in the $\nu(M-Cl)$ region were observed for *cis-*dichloro-compounds, only in two instances [*cis-*$(PMe_3)_2PtCl_2$ and *cis-*$(PMe_3)_2PdMe_2$] were two metal–phosphorus bands observed. Metal–donor bands are generally much less intense than metal–halogen (stretching) bands, and the weak component of a pair of bands could escape detection. Although metal–donor bonds are considerably more polar than metal–halogen bonds, the infrared intensity depends on the rate of change of bond moment with bond length and, whereas extension of a metal–halogen bond would in the limit give a very highly polar ion-pair (M–X $\longrightarrow$ $M^+ + X^-$), extension of a metal–donor bond would presumably give two neutral species (M$\Leftarrow$L $\longrightarrow$ M + :L).

Not only are two or more metal–chlorine stretching bands observed in *cis-*dichlorides, in contrast to the single $\nu(M-Cl)$ of *trans-*dichlorides, but the frequencies of the *cis-*dichlorides are very considerably less. In the palladium series $\nu(Pd-Cl)$ is in the range 269—335 cm.$^{-1}$ for *cis-*complexes and varies considerably with the donor group present in the molecule, whereas for the *trans-*complexes $\nu(Pd-Cl)$ is found in a very narrow range 353—359 cm.$^{-1}$ independent of the donor (except the *trans-*diammine). These two differences provide another way of distinguishing between *cis-* and *trans-*configurations. That metal–chlorine stretching frequencies should be lower in *cis-* than in *trans-*complexes is to be expected on the basis of Chatt's theory of partial d_π-bonding between metal and ligand (see, for example, ref. 19).

The spectrum of cæsium tetrachloropalladate(II), Cs_2PdCl_4, contains a single band at 327 cm.$^{-1}$, which is within the range observed for *cis-*dichloropalladium complexes. Adams[18] observed a band at 320·5 with a shoulder at 328 cm.$^{-1}$ in the spectrum of K_2PtCl_4.

It is interesting that both the bistrimethylphosphine and the bistrimethylarsine complex

[19] Chatt and Wilkins, *J.*, 1952, 4300; Chatt, Duncanson, and Venanzi, *J.*, 1955, 4456.

of palladium(II) chloride have the *cis*-configuration in the solid state, whereas the higher homologues all have *trans*-structures. Mann and Purdie [20] concluded on the basis of the colour and the pyro- and piezo-electric effects observed with crystalline $(AsMe_3)_2PdCl_2$ that it may exist in the solid state in the form of the *cis*-isomer. Dichlorobistrimethyl-phosphinepalladium has a very pale yellow colour, in contrast to the bright yellow of the higher homologues of undoubted *trans*-structure. We found, however, that extraction with chloroform of the crude complex gave a very pale yellow solid and a bright orange solution. Rapid evaporation of the chloroform solution gave a bright orange solid, which, beyond reasonable doubt, was the *trans*-isomer but became very pale yellow within a minute at room temperature.

EXPERIMENTAL

Most of the complexes studied were prepared by methods described in Gmelin's "Handbuch." The nickel complexes of trimethylphosphine were prepared by Beg and Clark's method; [21] for a description of the other nickel complexes see ref. 22. In the preparation of gold(III) bromide by Colles and Gibson's method [23] it was found better to omit the glass beads. The organogold(I) compounds are described separately. [2]

Bis(trimethylgold)ethylenediamine, prepared according to Gilman and Woods, [1] was found to decompose quickly in ether solution at room temperature, the solution becoming blue.

Trimethyl(trimethylphosphine)gold(III), PMe_3AuMe_3.—Trimethylphosphine (an excess of a solution in ether) was added to the ethylenediamine complex, $(Me_3Au)_2en$ (0·5 g.), in ether (10 c.c.) at $-20°$. After the addition of water (10 c.c.) the ether layer was separated and the ether removed by pumping, giving an oil which solidified below 0°. Sublimation at room temperature and *ca.* 0·004 mm. on to a cold finger at $-78°$ gave a colourless *product*, m. p. 23° (Found: Au, 61·6. $C_6H_{18}AuP$ requires Au, 61·9%).

Trimethyl(triphenylphosphine)gold(III), PPh_3AuMe_3.—Triphenylphosphine (6·8 g., 0·026 mole) in ether (20 c.c.) was added to trimethylgold [from gold(III) bromide, 11·3 g., 0·026 mole] in ether (150 c.c.) at $-65°$. The mixture was stirred for 45 min., and water (50 c.c.) was added after the mixture had warmed to room temperature. After removal of gold (2·4 g.) the *complex* was separated from the excess of triphenylphosphine chromatographically on alumina, and was crystallised from hexane; it (5·3 g., 41%) had m. p. 120° (decomp.) (Found: C, 50·2; H, 5·0; Au, 39·5%; *M*, cryoscopic in 2·44, 3·91, 4·89 wt. % benzene, 499, 496, 501. $C_{21}H_{24}AuP$ requires C, 50·0; H, 4·8; Au, 39·1%; *M*, 505).

Thermal Decomposition.—Trimethyl(triphenylphosphine)gold(III) (0·3516 g.) was heated for $\frac{1}{2}$ hr. at 120° in a vessel attached to a vacuum-apparatus. Ethane (20·64 c.c. at S.T.P., equiv. to 87% of the methyl groups originally present) was collected and identified by its infrared spectrum. Neither methane nor ethylene could be detected. Metallic gold and triphenylphosphine (m. p. 79°) were recovered from the involatile residue.

Ethane (4·15 c.c. at S.T.P.) was collected after the same complex (0·1646 g.) had been heated in xylene solution for $\frac{1}{2}$ hr. at 120°. Methyl(triphenylphosphine)gold(I) (identified by m. p., 175°, and infrared spectrum) was recovered from the xylene solution.

Methyl(triphenylphosphine)gold(I) (0·2700 g.), heated for $\frac{1}{2}$ hr. at 175°, gave ethane (5·79 c.c. at S.T.P., corresponding to 95% of available methyl), gold, and triphenylphosphine; and 0·4568 g., heated for $\frac{1}{2}$ hr. at 175° in biphenyl (5 g.), gave ethane (5·49 c.c. at S.T.P.) corresponding to 48% of the available methyl. We did not attempt to detect methylated biphenyls.

Infrared spectra were measured with Grubb-Parsons double-beam grating spectrometers; a GS2A instrument was used for wavelengths below 22 μ; and a DB3/DM2, with a 200-line per cm. grating blazed for 45 μ, for wavelengths between 22 and 50 μ. The wavelength calibration in the last region was checked against part of the rotational spectrum of water vapour, [24] the spectrometer being used as a single-beam instrument. In this region Nujol mulls generally give good spectra with little light scattering. Unless stated otherwise, specimens were examined in the form of Nujol mulls mounted between cæsium iodide discs. Halogen exchange with

[20] Mann and Purdie, *J.*, 1935, 1549.
[21] Beg and Clark, *Canad. J. Chem.*, 1961, **39**, 595.
[22] Cass, Coates, and Hayter, *J.*, 1955, 4007.
[23] Colles and Gibson, *J.*, 1931, 2411.
[24] Randall, Dennison, Ginsburg, and Weber, *Phys. Rev.*, 1937, **52**, 160.

cæsium iodide can be troublesome, and in the case of chlorides and bromides thin Polythene sheets were placed between the mulls and the cæsium iodide.

Dipole Moments.—These were measured for benzene solutions, refractivities being measured at 5893 Å. Atom polarisation was taken as 10 c.c. for gold(I) compounds (two ligands) and 20 c.c. for gold(III) compounds (four ligands), on the basis of data obtained on non-polar palladium [4] and platinum [3] compounds. Moments were calculated from observed weight fractions, densities, refractivities, and changes of capacity by Halverstat and Kumler's method.[25]

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Trimethyl(triphenylphosphine)gold(III).			
0·005326	1·14131	561·6	0·214
0·009655	1·13868	—	0·416
0·014038	1·13625	1431	0·617
0·015777	1·13548	1685	0·691

$_T P = 691,\ _E P = 115,\ _0 P = 556$ c.c., $\mu = 5\cdot2$ D.

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Trichloro(triethylphosphine)gold(III).			
0·002694	—	—	0·459
0·003415	1·14185	—	0·569
0·003685	1·14103	—	—
0·004102	—	—	0·690
0·004198	1·14050	—	—
0·004957	1·13981	—	0·775

$_T P = 1978,\ _E P = 68$ (calc.), $_0 P = 1890$ c.c., $\mu = 9\cdot6_2$ D.

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Tribromo(triethylphosphine)gold(III).			
0·002754	—	—	0·349
0·004428	—	362·3	0·579
0·006342	1·13840	525·3	0·772
0·006928	1·13753	—	—
0·007887	1·13678	652·2	0·991
0·010738	—	887·7	1·281
0·013143	1·13238	—	—

$_T P = 1942,\ _E P = 74,\ _0 P = 1848$ c.c., $\mu = 9\cdot5_0$ D.

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Tri-iodo(triethylphosphine)gold(III).			
0·002047	—	—	0·175
0·004795	1·13987	—	—
0·005984	—	—	0·504
0·007313	1·13744	—	—
0·009712	1·13489	—	0·795
0·013473	1·13179	—	1·115

$_T P = 1639,\ _E P = 85$ (*calc.*), $_0 P = 1534$ c.c., $\mu = 8\cdot6_9$ D.

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Chloro(triethylphosphine)gold(I).			
0·002281	—	—	0·249
0·004293	1·14056	—	0·649
0·007246	1·13756	—	1·083
0·009541	1·13666	—	1·309
0·013473	1·13362	561·6	—
0·014404	—	597·8	—
0·016545	—	688·4	—
0·021493	—	869·6	—

$_T P = 1497,\ _E P = 52,\ _0 P = 1435$ c.c., $\mu = 8\cdot3_8$ D.

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Bromo(triethylphosphine)gold(I).			
0·003698	1·14075	—	0·459
0·004714	1·13987	—	0·625
0·007589	1·13802	—	1·005
0·010976	1·13439	434·8	1·449
0·013849	—	652·2	—
0·016866	—	760·9	—
0·018654	—	869·6	—

$_T P = 1490,\ _E P = 56,\ _0 P = 1424$ c.c., $\mu = 8\cdot3_5$ D.

Wt. fraction (w)	Spec. volume (v)	$10^6 \Delta n$	ΔC (cm.)
Iodo(triethylphosphine)gold(I).			
0·004461	1·14056	—	0·530
0·009183	1·13669	452·9	1·072
0·012548	1·13386	616·0	1·493
0·016947	1·13072	—	—
0·016474	—	815·3	—

$_T P = 1494,\ _E P = 59,\ _0 P = 1425$ c.c. $\mu = 8\cdot3_5$ D.

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[25] Halverstat and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.