Vibrational and Nuclear Magnetic Resonance Spectroscopic Studies on some Carbonyl Complexes of Gold, Palladium, Platinum, Rhodium, and Iridium

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Detailed i.r. and Raman studies are reported for [AuCl(CO)], $[PtX_3(CO)]^-$ (X = Cl, Br, or I), $[PdX_3(CO)]^-$, *cis*-$[PtX_2(CO)_2]$, *cis*-$[RhX_2(CO)_2]^-$ (X = Cl or Br), and *cis*-$[IrCl_2(CO)_2]^-$ together with assignments. Skeletal stretching wavenumbers are reported for *cis*-$[PtX_2(CO)(PMe_3)]$ (X = Cl, Br, or I), *trans*-$[PtX(CO)(PMe_3)_2]^+$, *trans*-$[RhX(CO)(PMe_3)_2]$ (X = Cl or Br), and $[RhCl_3(CO)(PMe_3)_2]$. The results of ^{13}C n.m.r. studies on the carbonyl complexes are reported together with those from ^1H n.m.r. and ^1H-$\{^{31}P\}$ and ^1H-$\{^{195}Pt\}$ INDOR spectroscopy on the phosphine-containing complexes. The ^{195}Pt chemical shifts of $[PtX_3(CO)]^-$ from direct measurements are reported. The results are discussed with the assistance of stretching force constants for some of the simpler complexes.

WE have made extensive studies by means of vibrational and n.m.r. spectroscopy of complexes of the platinum metals containing trimethylphosphine, trimethylarsine, trimethylamine, *etc.*[1-5] The significance of π-acceptor properties in the bonding of phosphine ligands in such complexes has been questioned,[6] but there can be no doubt of the significance of the π-acceptor ability of carbon monoxide.

In this paper we report the results of a detailed analysis of the vibrational spectra of [AuCl(CO)] and the anionic complexes $[MX_3(CO)]^-$ ($M = Pt^{II}$ or Pd^{II}, X = halide). We have also studied the spectra of some bis(carbonyl) complexes of the type *cis*-$[MX_2(CO)_2]$ and some mixed carbonyl–phosphine complexes of platinum and rhodium so as to identify the skeletal stretching vibrations. N.m.r. spectroscopy (^1H, ^{13}C,

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^{1}H-{^{31}P}, ^{1}H-{^{195}Pt}, and ^{1}H-{^{103}Rh}) has been used to provide further information on these complexes.

RESULTS

Vibrational Spectra.—[AuCl(CO)]. The i.r. and Raman spectra in solution, as well as the Raman spectrum of the solid, were obtained. A complete unambiguous assignment, on the basis of $C_{\infty v}$ symmetry, is given in Table 1.

TABLE 1

Assignment for the vibrational spectra (cm^{-1}) of [AuCl(CO)] [a]

	I.r. (CH_2Cl_2)	Raman (solid)	Raman (C_6D_6)
^{12}CO str. Σ^+	2 162vs	2 183s	
^{13}CO str. Σ^+	2 114vw		
AuC str. Σ^+	443w	423w	445s, p
AuCO def. Π	416m	399w	415m, dp
Au^{35}Cl str. Σ^+	371s	358s	369s, p
Au^{37}Cl str. Σ^+	364m (sh)	345 (sh)	
ClAuC def. Π	95m, br [b]	96s	

[a] The descriptions of the CO stretching vibrations observed in the Raman take into account spectrometer sensitivity. [b] In benzene solution.

Complex anions $[MX_3(CO)]^-$. The first report purporting to account in detail for the spectra of $[PtCl_3(CO)]^-$ was by Denning and Ware.[7] We have subsequently shown that their Raman measurements were made on a solution which was a mixture of this anion with $[Pt_2Cl_4(CO)_2]^{2-}$.[8] Cleare and Griffith [9] reported the spectra of the set of platinum anions. However, there are a large number of (mostly) minor discrepancies between the spectra of the chloro- and bromo-anions which are included in both their papers for which they offered no comment. They gave little discussion of their assignments with which we are not in full agreement so we will reconsider these spectra together with those of $[PdX_3(CO)]^-$ (X = Cl or Br) which have been isolated for the first time. The spectra in the 1 700—2 300 and <650 cm^{-1} regions observed for solutions as well as the solid state are presented in Table 2.

For C_{2v} symmetry there should be three vibrations in the 400—600 cm^{-1} region: MC stretching and in-plane and out-of-plane MCO deformations. The i.r. spectra of the platinum bromo- and iodo-anions in solution showed three such bands, the weakest of which must relate to MC stretching since it corresponds to a polarised Raman feature. In the spectra of the other three complexes the MC stretching and one of the bending vibrations are coincident in solution although slightly separated for the solid state. The MCO deformation frequencies of $[PtX_3(CO)]^-$ are close to those of *cis*-$[PtCl_2Me(CO)]^-$ where depolarisation ratios show that the one at higher wavenumber is the in-plane mode.[10] Consequently we assign them and those of $[PdX_3(CO)]^-$ in the same order, although this is the reverse of the order given by Gribov *et al.*[11] for *cis*- and *trans*-$[PtCl_2(CO)(NH_3)]$. These deformations gave rise to, at best, weak Raman features.

The assignments of MX stretching vibrations follow from the intensity patterns that we have previously established for $[MX_3L]^-$.[1] The spectra of $[PtCl_3(CO)]^-$ showed four features in the region expected for deformations about platinum. That at highest wavenumber has relatively high Raman intensity and can therefore be related to the in-plane scissors vibration of $[MX_4]^{2-}$ (B_{2g}) [12] or of *trans*-$[MX_2L_2]$.[1] As the mass of CO must be approaching that of chlorine, it is likely that the other deformations will show some resemblance to those of $[PtCl_4]^{2-}$. Thus, the strong i.r. feature at 131 cm^{-1} in solution is probably an out-of-plane deformation related to A_{2u}, whilst the lowest feature (105 cm^{-1}) is close to the frequency calculated for the inactive B_{2u} mode of $[PtCl_4]^{2-}$.[12] The remaining feature near 150 cm^{-1}, which is possibly polarised in the Raman, corresponds to the E_u in-plane motion and may be either or both of the A_1 and B_1 modes here. This region for $[PdCl_3(CO)]^-$ can be assigned similarly, but for the complexes of the heavier halides there are less features.

Complexes cis-$[MX_2(CO)_2]$. Only the i.r. features in the CO stretching region have been previously reported for the platinum complexes.[13,14] We studied the lower region of the i.r. spectra using benzene solutions, and obtained the Raman spectra of the solids and benzene solutions saturated at 60 °C. The structurally similar anions, $[RhX_2(CO)_2]^-$ and $[IrCl_2(CO)_2]^-$, were examined, primarily to obtain solution data to supplement earlier studies.[9,15] Our assignments (Table 3) for the 400—700 cm^{-1} region assume that the strongest Raman features relate to MC stretching vibrations and the strongest i.r. bands to MCO bending modes. For the latter, both the in-plane modes and only one of the out-of-plane modes are i.r. active. Two of the observed bands are quite close together for all the complexes but the third is *ca.* 70—110 cm^{-1} higher, the separation being largest when the C≡O stretching wavenumbers indicate greatest back donation from the metal to CO. We conclude that the out-of-plane MCO deformation modes are at higher wavenumbers than the in-plane ones in these bis(carbonyl) systems.

Complexes containing CO *and* PMe_3. The skeletal stretching frequencies of $[PtX_2(CO)(PMe_3)]$ (X = Cl, Br, or I), $[PtX(CO)(PMe_3)_2]^+$, $[RhX(CO)(PMe_3)_2]$ (X = Cl or Br), and two isomers of $[RhCl_3(CO)(PMe_3)_2]$ are given in Table 4. Full documentation of the spectra may be found in Supplementary Publication No. SUP 22116 (8 pp.).*

The CO stretching frequencies of complexes $[PtX_2(CO)L]$ have been reported [13,16] where L is one of a variety of donors including phosphines but not trimethylphosphine. The ^{1}H n.m.r. spectra, and i.r. spectra of the CO stretching region, indicate that essentially only one isomer is present in solution although for the iodo-complex there is slight contamination by its decomposition product, $[Pt_2I_4(PMe_3)_2]$. The MX_2 stretching features do not correspond to a *trans* arrangement, and for the chloro-complex both were polarised in the Raman spectrum confirming a *cis*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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TABLE 2

Infrared and Raman spectra (cm^{-1}) of $[MX_3(CO)]^-$ (MX = PtCl, PtBr, PtI, PdCl, or PdBr) [a,b]

	$[NPr^n_4][PtCl_3(CO)]$				$[NBu^n_4][PtBr_3(CO)]$				$[NBu^n_4][PtI_3(CO)]$				$[NBu^n_4][PdCl_3(CO)]$				$[NBu^n_4][PdBr_3(CO)]$			
	I.r.		Raman		I.r.		Raman		I.r.		Raman		I.r.		Raman		I.r.		Raman	
	mull	solution [c]	solid	CH_2Cl_2	mull	solution [c]	solid	CH_2Cl_2	mull	solution [c]	solid	CH_2Cl_2	mull	solution [c]	solid	CH_2Cl_2	mull	solution [c]	solid	CH_2Cl_2
^{12}CO str. A_1	2 083vs	2 098vs	2 083vs	2 095vs, p	2 083vs	2 089vs	2 082vs	2 090vs, p	2 066vs	2 078vs			2 120vs	2 132vs	2 116vs	2 130vs, p	2 112vs	2 120vs		2 118vs,p
^{13}CO str.	2 038w	2 050w			2 037w	2 043w			2 020w	2 029w			2 071w	2 084w			2 062w	2 072w		
MC str. A_1	504 (sh)		507m	497m, p	504wm	496(sh)	505m	496wm, p	492w	492w	492m	492m, p			422w	416w, p			424wm	413wm, p
MX str. A_1	*325*m	*322m*	*324m*	322m, p	*227*m	*228*s	*229*s	*227*ms, p	*178*m	*178*m	*178*ms	*178*ms, p	*332*m	*334*m	*329*m	*329*m, p	*232*m	*232*ms	*232*m	*228*m, p
MX_2 str. A_1			*348*s	*345*s, p	*204*w	*204*wm	*207*vs	*204*vs, p	*151*w	*150*w	*151*vs	*150*vs, p	*299*wm	*300*wm	*299*s	*d*	*191*w	*190*w	*191*vs	*187*vs, p
MX_2 str. B_1	*344*s	*344*s			*245*s	*246*vs			*200*ms	*202*s	*200*w		*350*s	*350*s	*348*w		*267*s	*267*s		
MCO in-plane def. B_1	543s	540s		539vvw	528s	525s	528vw	525vw	509s	510s	510w		474m	475m	481vw		463s	462s	460vw	
MCO out-of-plane def. B_2	508m	497ms			486ms	484m			472m	470m			427w	423wm			415wm	414m		
Skeletal defs.																				
B_1	164w	*ca.* 170vw (sh)	163s	166m, dp			106s	100m, dp			80ms	80ms, dp	156vw		154m	157m, dp			95m	90m, dp
B_1 and/or A_1	151wm	152w	150vw	152vw, p?	112w								140w (sh)	146w (sh)			110 (sh)			
B_2	129m	131s			98w	100wm, br			90wm	90w, br			127m	130m	126vw		100w	85wm, br		
B_2			105m	105m, dp									105vvw		*ca.* 104 (sh)					
Lattice	58m, br				76vw 59w, br				45w, br				60w, br				56w, br			
Other bands	497 (sh)	512 (sh)	496 (sh)	571vvw	545vw				530 (sh)				484 (sh)		254w, br		530w			
			308w, (sh)		511vw				521 (sh)	520w										
Limit of study	(30)	(80)	(50)	(110)	(20)	(70)	(60)	(60)	(20)	(70)	(60)	(60)	(25)	(80)	(80)	(110)	(25)	(70)	(65)	(75)

[a] As in Table 1. [b] Cation bands omitted. [c] In CH_2Cl_2 above 250 cm^{-1} and in $CHCl_3$ (EtOH free) below 250 cm^{-1}. [d] Obscured by solvent.

TABLE 3

Infrared and Raman spectra (cm^{-1}) of *cis*-$[PtX_2(CO)_2]$ (X = Cl or Br) and *cis*-$[MX_2(CO)_2]^-$ (MX = RhCl, RhBr, or IrCl) [a,b]

	$[PtCl_2(CO)_2]$			$[PtBr_2(CO)_2]$			$[NPr^n_4][RhCl_2(CO)_2]$				$[NPr^n_4][RhBr_2(CO)_2]$		$[NPr^n_4][IrCl_2(CO)_2]$			
	I.r. [c]	Raman		I.r.	Raman		I.r.		Raman		I.r.		I.r.		Raman	
	benzene	solid	benzene	benzene	solid	benzene	mull	CH_2Cl_2	solid	CH_2Cl_2	mull	$CDCl_3$	mull	CH_2Cl_2	solid	CH_2Cl_2
$(^{12}CO)_2$ str. sym	2 178vs	2 185vs	2 172vs, p	2 164vs	2 173vs	2 162vs, p	2 069vs	2 070vs	2 062s	2 069vs, p	2 067vs	2 068vs	2 055vs	2 056s	2 052vs	2 056vs, p
$(^{12}CO)_2$ str. asym	2 137vs	2 144ms	2 131m, dp	2 122vs	2 133m 2 125m	2 121m, dp	1 996vs	1 994vs	1 979s	1 990vs, dp	1 995vs	1 993vs	1 977vs	1 973vs	1 962s	1 973vs, dp
Other CO region bands	2 148 (sh)			*ca.* 2 130 (sh)			2 046w	2 035vw			2 044w		2 043 (sh)			
	2 093w 2 083 (sh)			2 086w			1 957w	1 940vw			1 957w		1 936 (sh)			
$M(CO)_2$ out-of-plane def.	539s			528s			622vs 598w (sh)	*d* *d*	599w	600w	609vs 584 (sh)	607vs	636m, br 568vw	638m		
$M(CO)_2$ in-plane def.	472ms 462m			460s 450ms			517m 496vs	510w (sh) 492vs	513w		514m 496vs	512w 486vs	528m, br 513s	528m, br 513wm		
MC_2 str. sym		460m	459m, p		453m	454m, p	492vs		493vs	496vs, p	487vs		542s	540m	542s	547s, p
MC_2 str. asym	430vw	430w			421w		464w		461s	455m, dp	449m	447w			526m	526wm, dp
MX_2 str. sym	*374*ms	*368*s	*374*s, p	*252*ms	*251*vs	*252*vs, p	*324*s	*317*vs	*324*s	*314*m, p	*231*ms	*227*s	*331*s	*329*s	*331*s	*329*s, p
MX_2 str. asym	*352*s	*344*m	*352*w, dp	*236*s	*233*ms	*234*m, dp	*294*vs	*288*vs	*294*w	*d*	*207*s	*203*s	*300*s	*299*s	*ca. 310*w, br	*d*
Skeletal defs. and lattice	160m 135 (sh) 115ms 104vw? 85vw?	158s 114s	156m (sh)	80wm, br	125 (sh) 105vs		145w (sh) 120 (sh) 113m 66w, br		147s 107vs	146m, dp					156ms, br 122s, br *ca.* 46s	
Other bands		192w		550 (sh) 165vvw	196w	214w, p	376vw 342w (sh)		618w 315 (sh)	617w, p						
Limit of study	(60)	(90)	(150)	(60)	(70)	(150)	(40)	(200)	(130)	(130)	(200)	(200)	(200)	(200)	(40)	(160)

[a,b,d] as in previous Tables. [c] In $CDCl_3$ solution the CO stretches are at 2 177.5 and 2 136.8 cm^{-1} and binary combination frequencies are at 4 343 ($2A_1$), 4 287 ($A_1 + B_1$), and 4 257 cm^{-1} ($2B_1$).

structure. The separations between the two MX_2 vibrations parallel the differences between the MX stretching vibrations *trans* to PMe_3 [1] and *trans* to CO in $[PtX_3L]^-$, so we have used these descriptions in Table 4 although there must be some mixing between them. The solid-state spectra are more complex than those in solution for the CO stretching region and for the PtCl vibrations of the chloro-complex.

TABLE 4

Skeletal stretching wavenumbers for some platinum and rhodium complexes containing CO and PMe_3 [a]

	$[PtCl_2(CO)(PMe_3)]$	$[PtBr_2(CO)(PMe_3)]$	$[PtI_2(CO)(PMe_3)]$
^{12}CO	2 107	2 103	2 094
PtC	490	486	479
PtP	378	375	370
PtX (*trans* CO)	350	237	177
PtX (*trans* P)	308	196 [b]	158

	$[PtCl(CO)(PMe_3)_2]^+$	$[PtBr(CO)(PMe_3)_2]^+$	$[RhCl(CO)(PMe_3)_2]$	$[RhBr(CO)(PMe_3)_2]$
^{12}CO	2 111	2 111	1 965 [c]	1 961 [b]
MC	502	494	550 [d]	552 [b]
MP_2 sym	363 [d]	363 [d]	356 [d]	359 [b]
MP_2 asym	350	350	343 [b]	342 [b]
MX	350	240	303 [d]	195 [b]

	fac,cis-$[RhCl_3(CO)(PMe_3)_2]$		*mer,trans*-$[RhCl_3(CO)(PMe_3)_2]$ [e]
^{12}CO	2 094 [b]		2 077
RhC	461 [d]		468
RhP_2 sym	384 [d]		348
RhP_2 asym	367 [d]		355
RhCl (*trans* CO)	331 [d]		325
$RhCl_2$ (*trans* P) sym	258 [b]	$RhCl_2$ (*trans* Cl) sym	300
$RhCl_2$ (*trans* P) asym	242 [b]	$RhCl_2$ (*trans* Cl) asym	351

[a] In CH_2Cl_2 unless otherwise stated. [b] Solid state. [c] In hexane. [d] In $MeNO_2$. [e] In C_6H_6.

TABLE 5

N.m.r. parameters for some carbonyl complexes of gold, palladium, platinum, rhodium, and iridium

Complex	$\delta(^{13}C)$ [a]	$^1J(M^{13}C)$/Hz	$\delta(M)$ [b]	Solvent
$[AuCl(CO)]$	170.8			*c*
$[NBu^n_4][PdCl_3(CO)]$	163.4			*d*
$[NBu^n_4][PdBr_3(CO)]$	164.9			*d*
$[NBu^n_4][PtCl_3(CO)]$	152.0	1 732	1 260	*e*
$[NBu^n_4][PtBr_3(CO)]$	153.0	1 701	562	*e*
$[NBu^n_4][PtI_3(CO)]$	156.2	1 636	−947	*e*
$[PtCl_2(CO)_2]$	151.6	1 576		*f*
$[PtBr_2(CO)_2]$	152.0	1 566		*f*
$[NPr^n_4][RhCl_2(CO)_2]$	183.1	72		*e*
$[NPr^n_4][RhBr_2(CO)_2]$	183.4	72		*e*
$[NPr^n_4][IrCl_2(CO)_2]$	169.6			*e*
$[PtCl_2(CO)(PMe_3)]$ [g]	158.4	1 808	369	*h*
$[PtCl(CO)(PMe_3)_2][BF_4]$ [i]	160.4	1 813	62	*j*

[a] Carbon-13 data on some related platinum complexes may be found in W. J. Cherwinski, B. F. G. Johnson, J. Lewis, and J. R. Norton, *J.C.S. Dalton*, 1975, 1156. [b] P.p.m. to high frequency of 21.4 MHz when the resonance of $SiMe_4$ is taken as 100 MHz. [c] C_6D_6. [d] $CDCl_3$. [e] $(CD_3)_2CO$. [f] C_6D_6 at *ca.* 340 K. [g] $\delta(^{13}C)$ for PMe_3, 15.7 p.p.m.; $^1J(PC)$ 45.8, $^2J(PtC)$ 41.2, and $^2J(PC)$ 7.6 Hz. [h] CD_3NO_2. [i] $\delta(^{13}C)$ for PMe_3, 13.0 p.p.m.; $|^1J(PC) + {}^3J(PC)|$ 41.2, $^2J(PtC)$ 30.5, and $^2J(PC)$ 9.9 Hz. [j] CH_2Cl_2–$CDCl_3$.

N.m.r. measurements confirm the *trans* configuration of $[PtX(CO)(PMe_3)_2][BF_4]$ and $[RhX(CO)(PMe_3)_2]$ (X = Cl or Br) in solution, and the vibrational measurements do not indicate any change of structure in the solid state. For $[PtCl(CO)(PMe_3)_2]^+$ the PtCl stretching and PtP_2 asymmetric-stretching vibrations are coincident giving rise to the bands at 350 cm^{-1} in the i.r. and Raman (polarised), but with the analogous bromo-complex there is only an i.r. band at this frequency (PtP_2 asym.). The assignments for the rhodium(I) complexes are straightforward.[17–19]

When *trans*-$[RhCl(CO)(PMe_3)_2]$ was chlorinated in dichloromethane precipitation occurred and the ^1H n.m.r. spectrum showed that the product contained *cis* phosphines. Some of the strong i.r. bands between 240 and 330 cm^{-1} can be reasonably assigned as RhCl stretching vibrations. The absence of any strong i.r. band near 350 cm^{-1} or any strong Raman band near 300 cm^{-1}, typical respectively of the asymmetric- and symmetric-stretching vibrations of a linear Cl–Rh^{III}–Cl group, indicates a *facial* arrangement of the chlorine atoms.[3] The i.r. band at 331 cm^{-1} must be the RhCl (*trans* to CO) stretch (see above). The selection of the $RhCl_2$ (*trans* to P) frequencies is based on the comparison with *fac*-$[RhCl_3(PMe_3)_3]$.[3]

If the chlorination is carried out on a suspension of the rhodium(I) complex in benzene, most of the solid dissolves and n.m.r. shows that the complex in solution contains *trans* phosphines. The solution vibrational spectra clearly indicate a *trans*-$RhCl_2$ group. When the solvent is evaporated, the i.r. spectrum of the product shows that, whilst it is still largely the *mer,trans* form, it also contains some of the *fac,cis* isomer.

N.M.R. Spectra.—We recorded the ^{13}C Fourier-transform spectra of all the simple carbonyl species to obtain shifts and coupling constants (Table 5). The ^{13}C spectra of *cis*-$[PtCl_2(CO)(PMe_3)]$ and *trans*-$[PtCl(CO)(PMe_3)_2][BF_4]$ were

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also obtained as examples of the mixed phosphine–carbonyl complexes. The ^{13}C chemical shifts show no obvious relation with the differences in bonding between the various complexes (see below). There is a decrease of *ca.* 12 p.p.m. between comparable complexes of second- and third-row transition metals and if anything the shifts seem to be characteristic of the metal.

The ^1H n.m.r. spectra of *cis*-$[PtX_2(CO)(PMe_3)]$ show the expected doublet with ^{195}Pt satellites, whilst those of *trans*-$[PtX(CO)(PMe_3)_2]^+$, *trans*-$[RhX(CO)(PMe_3)_2]$, and *trans*-$[RhX_3(CO)(PMe_3)_2]$ are the typical ' triplet ' with a broad central line expected for an $[AX_9]_2$ spin system with large $^2J(PP)$. The *trans* disposition of the phosphine was further confirmed for the platinum complexes by the large positive values of $^2J(PP)$ obtained by ^1H-$\{^{31}P\}$ INDOR.[20]

TABLE 6

N.m.r. parameters of some carbonyl(trimethylphosphine) complexes of platinum and rhodium

Complex	τ(Me)	^2J(PH)/Hz [a]	^3J(MH)/Hz	δ(P) [b]	^2J(PP)/Hz	^1J(MP)/Hz	δ(M) [c]	Solvent
$[PtCl_2(CO)(PMe_3)]$	8.02	−12.8	+38.2	12.3		+2 760	369	*d*
$[PtBr_2(CO)(PMe_3)]$	7.96	−12.9	+39.0	12.1		+2 758	129	*d*
$[PtI_2(CO)(PMe_3)]$	7.90	−12.5	+39.8	15.2		+2 686	−395	*d*
$[PtBr(Cl)(CO)(PMe_3)]$ [e]	8.02	−13.0	+39.1	8.8		+2 760	238	*d*
[f]	7.95	−12.7	+38.0	15.9		+2 739	278	*d*
$[PtCl(I)(CO)(PMe_3)]$ [e]	8.08	−12.9	+39.1	8.3		+2 679	20	*d*
$[PtBr(I)(CO)(PMe_3)]$ [f]	8.01	−12.9	+39.2	8.5		+2 662	−122	*d*
$[PtCl(CO)(PMe_3)_2][BF_4]$	8.14	−8.6	+25.3	6.0	+377	+1 858	62	*g*
$[PtBr(CO)(PMe_3)_2][BF_4]$	8.08	−8.6	+25.3	10.7	+376	+1 846	−61	*g*
trans-$[RhCl(CO)(PMe_3)_2]$	8.77	−6.6	−1.0	10.6		−114	−415	*h*
trans-$[RhBr(CO)(PMe_3)_2]$	8.79	−6.8	−1.0	13.3		−113	−448	*h*
trans-$[RhCl_3(CO)(PMe_3)_2]$	8.63	−8.1	−0.5	1.9		−72	1 477	*h*
trans-$[RhBr_3(CO)(PMe_3)_2]$	8.53	−7.8	−0.5	14.6		−73	983	*h*
cis-$[RhCl_3(CO)(PMe_3)_2]$	8.11	12.0	0.8					*g*

[a] $|^2J(PH) + {}^4J(PH)|$ for *trans* complexes. [b] P.p.m. to low frequency of H_3PO_4. [c] P.p.m. to high frequency of 21.4 MHz for ^{195}Pt and 3.16 MHz for ^{103}Rh when the resonance of $SiMe_4$ is taken as 100 MHz. [d] CD_3NO_2. [e] Cl *trans* to CO. [f] Br *trans* to CO. [g] CH_2Cl_2. [h] C_6H_6.

Due to the very low solubility of *fac,cis*-$[RhCl_3(CO)(PMe_3)_2]$, the ^1H n.m.r. features required to ascertain $^2J(PP)$ could not be identified, only the two strong lines (with ^{103}Rh coupling) being visible with certainty.

The ^1H resonances of the phosphine complexes were used for ^1H-$\{^{31}P\}$, ^1H-$\{^{103}Rh\}$, and ^1H-$\{^{195}Pt\}$ INDOR measurements to obtain data for these nuclei (Table 6). The signs of the coupling constants are the same as found previously for trimethylphosphine complexes of platinum and rhodium.[4] The changes in the ^{195}Pt chemical shift of a complex when bromide is replaced by chloride or iodide (Δ_{Cl} or Δ_I respectively) are affected in a regular way by the other ligands present.[21] In order to obtain information about the effect of carbonyl on Δ_{Cl} and Δ_I, we extended our results for the three complexes *cis*-$[PtX_2(CO)(PMe_3)]$ by studying the mixed halogeno-species formed when any two of these complexes are allowed to equilibrate in solution. For the chloride–bromide system, the mixed halide isomer with bromide *trans* to phosphine was favoured over the other in the ratio *ca.* 8 : 1, whilst for the other two mixed systems only the isomer with iodide *trans* to phosphine was observed. From the values of δ(Pt), we calculated the effects of a *trans*-carbonyl group to be −172 and +345 p.p.m. respectively on Δ_{Cl} and Δ_I, which are similar to the results for a *trans* phosphine. The effects of a *cis*-carbonyl group are +14 and +16 p.p.m. respectively and these parameters reproduce the differences between the anions $[PtX_3(CO)]^-$ (X = Cl, Br, or I) to within 3%.

The ^{195}Pt chemical shifts of a series of anions, $[PtX_3L]^-$, have been related to their electronic-excitation energies *via* the equation derived by Ramsey for the dominant paramagnetic contribution, but only after the inclusion of a coefficient for each of the four donor atoms.[21] The visible–u.v. spectra of the carbonyl analogues in dichloromethane showed the following features [peak maxima in 10^3 cm^{-1}, intensities (dm^3 mol^{-1} cm^{-1}) in parentheses]: $[NBu^n_4][PtCl_3(CO)]$, 24.2 (35), *32.1* (700), *35.5* (1 400), 39.4 (4 700); $[NBu^n_4][PtBr_3(CO)]$, *31.1* (200), *34.6* (2 600), 38.2 (2 600); $[NBu^n_4][PtI_3(CO)]$, 23.8 (640), *27.6* (3 400), *33.3* (3 300), 36.6 (5 000). Using the italicised values for the $^1A_{1g}\rightarrow{}^1A_{2g}$ and $^1A_{1g}\rightarrow{}^1E_g$ transitions and the previously obtained values [21] for the coefficients of Cl, Br, and I, the mean coefficient for carbonyl is 0.99 relative to Cl, *i.e.* effectively the same as for chloride. This is much less than the coefficient for NMe_3, the only other first-short-period donor we have investigated, but greater than the value for PMe_3 and SMe_2 (0.82). Lower values of the coefficient probably follow from greater covalency of σ and π bonds between the metal and the donor.

DISCUSSION

The vibrational data presented here for complexes of the types $[MX_3(CO)]^-$ and $[MX_2(CO)_2]$ have been incorporated into force-constant calculations using a similar modified valence-force-field approach in each case and adopting constraints from studies of planar $[MX_4]^{2-}$ systems.[12] Fuller details will be presented elsewhere.[22,23] The stretching force constants obtained are listed in Table 7 together with those for [AuCl(CO)] calculated by Smith.[24]

The formal charges on $[PtCl_2(CO)_2]$ and $[IrCl_2(CO)_2]^-$ differ by one unit, although in practice this is likely to be

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[20] R. J. Goodfellow and B. F. Taylor, *J.C.S. Dalton*, 1974, 1676.

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[24] J. G. Smith, Ph.D. Thesis, Bristol University, 1967.

reduced somewhat by changes in the electron donation of the ligands between the two complexes. On going from platinum to iridium, f_{MC} increases by 48% while f_{CO} decreases by 17%. Similar effects are observed on alteration of the period of the metal, *e.g.*, between $[PtCl_3(CO)]^-$ and $[PdCl_3(CO)]^-$, f_{MC} decreases (40%) and f_{CO} increases (7%). The much greater response of f_{MC} than f_{CO} implies that the change in π bonding is only part of the effect on the MC bond.

The disfavouring of a heavy halide (with more covalent bonding to the metal) *trans* to carbonyl in *cis*-$[PtX(Y)(CO)(PMe_3)]$, the large reduction of the effect of the *trans* halide on δ(Pt) (a covalent contribution), and its coefficient for the relation of δ(Pt) to the excitation energies in $[PtX_3(CO)]^-$ all suggest that the metal–carbonyl bond is relatively covalent. The covalency of the M–C bond should be enhanced by the use of relatively low-energy orbitals on the metal, *i.e.* 6*s* or 5*d*. Although ^1J(PtC) increases between $[PtX_2(CO)_2]$ and $[PtX_3(CO)]^-$, the change is nothing like that in f_{MC} suggesting that the platinum 6*s* orbital is not especially significant, which leaves the $5d_{x^2-y^2}$ as the most important orbital for platinum–carbonyl bonding. The symmetric- and asymmetric-stretching vibrations of the *trans*-MCl_2 unit in $[PtCl_3L]^-$ show very little variation from 326 and 330 cm^{-1} respectively for trialkylphosphines, trialkylarsines,[1] dimethyl sulphide,[25] and trimethylamine.[26] However, when L is carbonyl there is a considerable increase in these frequencies. The good π-acceptor and weak σ-donor nature of carbon monoxide will result in a greater positive charge on the metal than for the other ligands and this will increase the Pt–Cl bond strength. The metal–halogen force constants imply a further increase in charge for $[PtX_2(CO)_2]$. Increasing the charge on the metal will particularly contract the 5*d* orbitals (the trend to hydrogenic orbitals). Thus the weakening of the platinum–carbonyl bond in $[PtX_2(CO)_2]$ probably arises from the reduced overlap of the carbonyl lone pair with the metal $d_{x^2-y^2}$ orbital and the competition between two carbonyl groups for this same orbital. The *d* orbitals are less extensive for the earlier period (Rh and Pd) and contract with increasing atomic number (Ir > Pt > Au), so reduced overlap for the M–C σ bond would also account for the lower metal–carbon force constants for complexes of the lighter metals and of gold.

Although the PtX stretching vibrations *trans* to CO are at especially high wavenumbers, much of this can be accounted for by the non-directional effect of the greater positive charge on the metal. If this is similar for the vibrational frequencies of both *cis*- and *trans*-PtCl bonds in $[PtCl_3(CO)]^-$, then the *trans* influence of carbon monoxide is similar to the weak ligands NMe_3 and SMe_2.[25,26] There is no great change in the PtC stretch for the sequence $[PtCl_3(CO)]^-$, *cis*-$[PtCl_2(CO)(PMe_3)]$, and *trans*-$[PtCl(CO)(PMe_3)_2]^+$ suggesting that the neutral phosphine donates to a similar extent to the chloride anion. Likewise, if chloride *cis* to PMe_3, *e.g.* Y in *trans*-$[PtCl(Y)(PMe_3)_2]$ or *cis*-$[PtCl_2Y(PMe_3)]$, is replaced by PMe_3 there is only a small decrease (*ca.* 5%) in ^1J(PtP) which contrasts with the large reduction (*ca.* 25%) when it is replaced by carbon monoxide.

TABLE 7

Stretching force constants (10^2 N m^{-1}) for some carbonyl complexes

	$[PtCl_3(CO)]^-$	$[PtBr_3(CO)]^-$	$[PtI_3(CO)]^-$	$[PdCl_3(CO)]^-$	$[PdBr_3(CO)]^-$
f_{CO}	16.45	16.33	16.13	17.58	17.36
f_{MC}	3.90	3.90	3.83	2.36	2.37
f_{MX_2}	2.02	1.83	1.60	1.79	1.61
f_{MX}	2.13	1.83	1.56	1.83	1.64

	$[PtCl_2(CO)_2]$	$[PtBr_2(CO)_2]$	$[RhCl_2(CO)_2]^-$	$[RhBr_2(CO)_2]^-$	$[IrCl_2(CO)_2]^-$	$[AuCl(CO)]$
f_{CO}	17.87	17.69	15.70	15.75	14.80	18.03
f_{MC}	3.06	2.93	3.21	3.07	4.53	2.55
f_{MX}	2.39	2.12	1.57	1.46	1.82	2.82

EXPERIMENTAL

Infrared and Raman measurements were made as previously reported.[1,26] The ^1H, ^1H-$\{^{31}P\}$, ^1H-$\{^{195}Pt\}$ n.m.r. spectra were obtained as in ref. 4. The ^{13}C n.m.r. spectra were measured with a JEOL PFT 100 spectrometer using a ^2H lock; the complexes were examined in the presence of chromium pentane-2,4-dionate as a shiftless relaxation agent. The ^{195}Pt chemical shifts of $[PtX_3(CO)]^-$ were obtained by direct observation by Dr. P. S. Pregosin (Eidgenössiche Technische Hochschule, Zürich) using a Bruker FX 90 Fourier-transform spectrometer as described elsewhere.[27]

Preparation of Complexes.—Analytical data are given in Table 8. The complex $[AuCl(CO)]$ was prepared as in ref. 28.

$[NR_4][MX_3(CO)]$. The salts $[NPr^n_4][PtX_3(CO)]$ (X = Cl or Br) were prepared by stirring a suspension of $[NPr^n_4]_2[Pt_2X_6]$ [26] (2 g) in nitromethane (20 cm^3) under an atmosphere of carbon monoxide until all the solid had dissolved and the solution had become yellow (*ca.* 2 h). Salts were precipitated by addition of diethyl ether, and were recrystallised from acetone by addition of ether and cooling. Yields were >90%. The salts $[NBu^n_4][PtI_3(CO)]$ and

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[27] W. Freeman, P. S. Pregosin, S. N. Sze, and L. M. Venanzi, *J. Magnetic Resonance*, 1976, **22**, 473.

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$[NBu^n_4][PdX_3(CO)]$ (X = Cl or Br) were prepared in a similar way except that dichloromethane was used as the reaction medium. Yields were quantitative.

$[PtX_2(CO)_2]$ (X = Cl *or* Br). Carbon monoxide was passed (2 h) down a long vertical tube on to $[PtX_2]$ at 220 °C. The product sublimed on to the cooler parts of the tube as long white needles. The complexes were quickly transferred to dry ampoules, sealed, and stored in a refrigerator. Yields *ca.* 70%.

Tetra(n-propyl)ammonium dicarbonyldichlororhodate(I). This salt was prepared by stirring sodium hexachlororhodate(III) (3 g) in concentrated hydrochloric acid (15 cm^3) under an atmosphere of CO (2 d). After 1 d a dark brown sludge formed, but over the second day all the solid dissolved to give a very pale yellow solution. Tetra(n-propyl)ammonium chloride (2 g) in dichloromethane (30 cm^3) was added and, after shaking, the organic layer was separated and dried with $Mg[SO_4]$. The pale yellow product crystallised on addition of diethyl ether, yield 90%. The dibromo-analogue was prepared by stirring a suspension of the chloride in concentrated hydrobromic acid (0.5 h). The mixture was extracted with dichloromethane as for the chloro-complex, yield 60%.

TABLE 8

Characterisation of complexes

Complex	Colour	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N	X
$[NPr^n_4][PtCl_3(CO)]$	Greenish yellow	127	30.25 (30.25)	5.8 (5.9)	2.9 (2.9)	15.0 (14.75)
$[NPr^n_4][PtBr_3(CO)]$	Yellow	121	28.8 (28.9)	4.9 (5.15)	1.8 (2.0)	
$[NBu^n_4][PtI_3(CO)]$	Orange	128	24.05 (24.15)	4.3 (4.3)	1.65 (1.65)	
$[NBu^n_4][PdCl_3(CO)]$	Orange	95 [b]	42.55 (42.25)	7.5 (7.5)	3.3 (2.95)	21.75 (22.0)
$[NBu^n_4][PdBr_3(CO)]$	Red	120 [b]	33.2 (33.1)	5.9 (5.9)	2.2 (2.25)	
$[NPr^n_4][RhCl_2(CO)_2]$	Pale yellow	116—120 [b]	40.2 (40.4)	6.8 (6.8)	3.45 (3.35)	
$[NPr^n_4][RhBr_2(CO)_2]$	Yellow	104—108 [b]	33.6 (33.3)	5.75 (5.6)	2.9 (2.75)	
$[NPr^n_4][IrCl_2(CO)_2]$	Pale yellow	112—113 [b]	33.0 (33.25)	5.6 (5.6)	2.7 (2.8)	
$[PtCl_2(CO)(PMe_3)]$	White	196—198	13.05 (13.0)	2.5 (2.45)		19.15 (19.2)
$[PtBr_2(CO)(PMe_3)]$	White	204—206	10.35 (10.4)	2.05 (1.95)		35.0 (34.8)
$[PtI_2(CO)(PMe_3)]$	Yellow	280 [b]	8.8 (8.6)	1.75 (1.6)		44.2 (45.8)
$[PtCl(CO)(PMe_3)_2][BF_4]$	White	168—170	17.0 (16.85)	3.75 (3.6)		
$[PtBr(CO)(PMe_3)_2][BF_4]$	White	165—170	15.95 (15.5)	3.35 (3.3)		
$[RhCl(CO)(PMe_3)_2]$	Pale yellow	108 [b]	26.6 (26.4)	5.8 (5.65)		
$[RhBr(CO)(PMe_3)_2]$	Pale yellow	111—112 [b]	23.6 (23.15)	5.1 (5.0)		
$[RhCl_3(CO)(PMe_3)_2]$	Yellow	130 [b]	22.1 (22.55)	4.6 (4.6)		

[a] Calculated values are given in parentheses. [b] With decomposition.

Tetra(n-propyl)ammonium dicarbonyldichloroiridate(I). Hydrated iridium trichloride (1.5 g) in 2-methoxyethanol (150 cm^3) and water (15 cm^3) was heated under reflux (*ca.* 6 h) under a slow stream of carbon monoxide to give a pale yellow solution (*cf.* ref. 29). The salt $[NPr^n_4]Cl$ (1.2 g) in water (30 cm^3) was added and the product extracted into dichloromethane. After drying the extract over $Mg[SO_4]$, crystallisation occurred on addition of diethyl ether, yield 50%.

$[PtX_2(CO)(PMe_3)]$ (X = Cl, Br, *or* I). A suspension of $[Pt_2X_4(PMe_3)_2]$ in dichloromethane was stirred under an atmosphere of carbon monoxide until all the solid had dissolved (2 d). The volume of solvent was reduced using a rotary evaporator and the complexes crystallised by addition of diethyl ether. Yield quantitative.

$[PtX(CO)(PMe_3)_2][BF_4]$ (X = Cl *or* Br). A suspension of $[Pt_2X_2(PMe_3)_4][BF_4]_2$ in acetone was stirred under an atmosphere of carbon monoxide (0.5 h). The solvent was removed on a rotary evaporator. The residue was dissolved in dichloromethane and boiled with charcoal for 5 min. After filtering, diethyl ether was added to crystallise the product. Yield quantitative.

Carbonylchlorobis(trimethylphosphine)rhodium(I). The complex $[Rh_2Cl_2(C_2H_4)_4]$ (0.04 mol) and dichloromethane (20 cm^3) were frozen in liquid nitrogen *in vacuo* and PMe_3 (*ca.* 0.08 mol), generated by heating $[AgI(PMe_3)]$ (0.085 mol), was condensed on to the surface. The mixture was allowed to warm to room temperature and was stirred overnight to yield an orange solution. The solution was stirred under a carbon monoxide atmosphere for 8 h whereupon it became yellow. The solvent was evaporated and the solid recrystallised from light petroleum (b.p. 40—60 °C) to give pale yellow crystals, yield 90%. The bromo-analogue was prepared by warming the chloro-complex with excess of NaBr in acetone (10 cm^3), removing the solvent, and recrystallising from light petroleum, yield 60%.

fac,cis-*Carbonyltrichlorobis(trimethylphosphine)rhodium*(III). This complex was prepared by bubbling chlorine into a dichloromethane solution of *trans*-$[RhCl(CO)(PMe_3)_2]$. The yellow precipitate was filtered off and washed with diethyl ether, yield 80%. Solutions of *trans,mer*-$[RhX_3(CO)(PMe_3)_2]$ (X = Cl or Br) were prepared by the addition of a stoicheiometric quantity of the dihalogen in benzene to a benzene suspension of the rhodium(I) complex.

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