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COORDINATIVELY UNSATURATED *o*-QUINONE COMPLEXES OF IRIDIUM(III) AND THEIR ROLE IN THE ISOMERIZATION OF OCTAHEDRAL COMPLEXES

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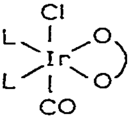
Summary

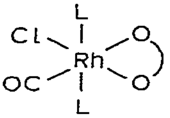
The oxidative addition reaction of tetrachloro-1,2-benzoquinone with *trans*-$\{IrCl(N_2)[P(C_6H_5)_3]_2\}$ yields the coordinatively unsaturated complex $\{IrCl(o\text{-}O_2C_6Cl_4)[P(C_6H_5)_3]_2\} \cdot C_6H_6$. Carbonylation of this complex can be used to prepare two isomers of formula $\{IrCl(o\text{-}O_2C_6Cl_4)(CO)[P(C_6H_5)_3]_2\}$. These are both different than the isomer obtained by Balch and Sohn from the oxidative addition of the quinone to Vaska's compound. The role of coordinatively unsaturated intermediates in the isomerization reactions of the octahedral carbonyl complexes will be discussed. The five coordinated *o*-quinone complex reacts with water to give an aquo complex. Two criteria for distinguishing *cis*- and *trans*-$M[P(C_6H_5)_3]_2$ geometries from intensities of IR bands in the regions 1570—1590 and 530—550 cm^{-1} have been tested for octahedral complexes. *cis*-Ph_3P octahedral complexes of iridium(III) have a band of high intensity in the 534—541 cm^{-1} region. There is no systematic relationship between the band intensities in the 1570—1590 cm^{-1} region and phosphine geometry.

Introduction

Five-coordinated complexes in which the metal has an nd^6 configuration are coordinatively unsaturated [1]. Their electron deficient character renders them highly reactive hence they are normally encountered only as reactive intermediates in a reaction sequence [1]. We [2—7] and others [8—10] have prepared a number of isolable five-coordinated iridium(III) complexes and have used them as models for steps in carbon monoxide insertion [3,4,9], desulfonylation [5,8], orthometalation [6], ligand substitution reactions [7,10], and isomerization reactions of octahedral complexes [10]. Previously work has led to the generalization that the 5-coordinate complexes are square pyramidal in geometry with the ligand of highest *trans* influence in the apical position [6,10]. Most of the examples prepared to date have been of the type [IrL_2X_2R] (L = tertiary phosphine, X = halide and R = H, CH_3, C(O)R′, $S(O)_2R''$). Both the groups R and L are high in the *trans* influence series [11]. In order to extend our work we wished to introduce fewer ligands of high *trans* influence. Oxygen donor ligands of the diolato type were chosen since the chelate effect would help stabilize the Ir—O linkages and 1,2-benzoquinones are known to undergo oxidative addition reactions with low valent complexes. Since the work of Valentine and Valentine [12] on the photo-induced addition of 1,10-phenanthrenequinone to Vaska's complex, Balch and Sohn [13] have reported that the compound tetrachloro-1,2-benzoquinone, (abbreviated herein as *o*-$O_2C_6Cl_4$ or O—O) readily adds to iridium(I) and rhodium(I) complexes under thermal conditions. They observed that the reaction of this quinone with *trans*-[$M(CO)Cl(PPh_3)_2$] yielded different isomers for the rhodium and iridium complexes (compounds Ia and Ib, L = PPh_3). The relative geometry of the two triphenylphosphine ligands was established by analogy with the bis(methyldiphenylphosphine) complexes where ^1H NMR allows an unambiguous assignment of *cis*- and *trans*-phosphine arrangements [14]. Our interest in the synthesis and reactions of five coordinated, d^6 complexes prompted us to investigate the addition of *o*-$O_2C_6Cl_4$ to *trans*-[$IrCl(N_2)(PPh_3)_2$].



(Ia)



(Ib)

The need for a means of characterizing the relative geometry of the two triphenylphosphine ligands in the products of this work and octahedral complexes in general led us to test the correlations of IR band intensities in the region of 1560—1590 [15] or 530—540 cm^{-1} [16] with *cis*- or *trans*-orientation of triphenylphosphine groups that have been found in some platinum complexes of the type PtL_2X_2. We and others [8] have used the relative intensity of the pair of bands in the region 1595—1560 cm^{-1} to support assignment of *trans* geometry in complexes of the type [$IrL_2(CO)RX_2$]. However, since few octahedral complexes of iridium(III) with *cis*-triphenylphosphine ligands have been characterized there has been no firm correlation established. In the course of characterizing the new diolato complexes, we have obtained IR spectra of known examples of octahedral complexes having *cis*- as well as *trans*-PPh_3 ligands and looked in detail for possible correlations of spectral features with phosphine ligand arrangements.

Results and discussion

The two IR correlations developed in platinum(II) complexes for differentiating between *cis*- and *trans*-$M(PPh_3)_2$-geometries are based on relative intensities of bands. To attempt the same for octahedral complexes we have tabulated in Table 1 band position and the intensity (relative to a very strong band of approximately constant position, ~520 ± 5 cm^{-1}) from the spectra of triphenylphosphine complexes. In platinum(II) compounds, Mastin has found that the band at ca. 540 cm^{-1} is strong for *cis*-ML_2 and weak for *trans*-ML_2 geometries (L =

TABLE 1

CORRELATION OF IR BAND POSITION (cm^{-1}) AND INTENSITY (in parentheses)[a] WITH THE GEOMETRY OF THE ML_2 FRAGMENT ($L = PPh_3$) IN OCTAHEDRAL COMPLEXES

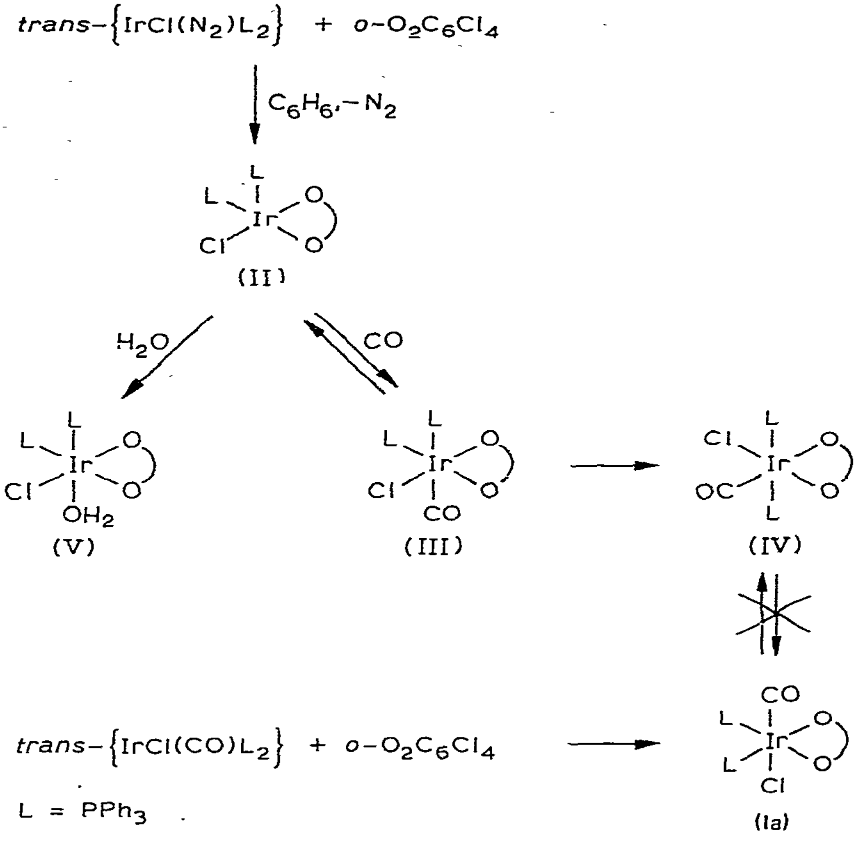
Compound	LML	1570—1590 cm^{-1} region	500—550 cm^{-1} region
$\{IrX(CO)L_2(TCNE)\}$			
X = Cl	*cis*	1584(10.8); 1572(13.9)	534(76.6)
X = Br[b]	*cis*	1585(13.9); 1572(10.2)	537(73.7)
$\{IrCl(CO)L_2(o\text{-}O_2C_6Cl_3)\}$[c] (Ia)	*cis*	1587(14.6); 1573(16.3)	539(82.6)
$\{RhCl(CO)L_2(o\text{-}O_2C_6Cl_4)\}$[c] (Ib)	*trans*	1586(12.7); 1570(18.2)	536(29.3)
$\{IrCl_2(CH_3)(CO)L_2\}$[d]	*trans*	1583(7.4); 1570(14.7)	[e]
$\{PtL_2(o\text{-}O_2C_6Cl_4)\}$	*cis*	1586(7.2); 1572(10.4)	550(96.0)
$\{IrCl(CO)L_2(o\text{-}O_2C_6Cl_4)\}$(III)	*cis*	1585(9.8); 1569(7.4)	538(85.9)
$\{IrCl(CO)L_2(o\text{-}O_2C_6Cl_4)\}$ (IV)	*trans*	1586(8.6); 1571(11.5)	536(sh)
$\{IrClL_2(o\text{-}O_2C_5Cl_4)H_2O\}$ (IV)	*cis*	1585(5.0); 1572(7.9)	541(79.1)

[a] Spectra were measured on Nujol mulls between CsI plates on an instrument recording in the transmittance (percent) mode. Intensities are given relative to that of a band at 520 ± 5 cm^{-1} which is taken as 100%. [b] Ref. 21. [c] Ref. 13. [d] Ref. 6. [e] No band observed, intensity = 0.

PPh_3) [16]. The data in Table 1 which compare well characterized *cis* and *trans* octahedral iridium and rhodium complexes suggests the correlation is also valid for these compounds. The relative intensity of the pair of bands at ca. 1585 and 1570 cm^{-1} does not depend systematically on phosphine geometry as can be seen by comparing $[IrCl(CO)L_2TCNE]$ and $[IrCl_2CH_3(CO)L_2]$.

The dinitrogeniridium complex reacts rapidly with $o\text{-}O_2C_6Cl_4$ in benzene to give a black solid for which the analysis is consistent with a solvate of formula $[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4)] \cdot C_6H_6$. The low solubility and great affinity for water prevented the determination of the molecular weight. A structure (II) is proposed (Scheme 1). The preference of five-coordinated d^6 compounds for square pyramidal geometry and occupation of the axial site by the ligand with the highest *trans* influence has been discussed before [6]. The position of ν(Ir—Cl) at 321 cm^{-1} (Table 2) is consistent with chlorine being *trans* to oxygen but not phosphorus [11b]. The ν(Ir—Cl) also suggests that the chloride is not acting as a bridging ligand since a lower frequency would be likely [11b]. The monomeric structure with phosphorus (greater *trans* influence than Cl) in the apical position is proposed. The facile reaction, to be discussed later in this paper, of the solid with moisture from the air to give an aquo complex also supports a monomeric structure. Balch and Sohn prepared the rhodium analog of II from $RhCl(PPh_3)_3$ [13].

Addition of carbon monoxide to the coordinatively unsaturated complex, at room temperature, gives a yellow carbonyl complex (III) in which the geometry of the remaining ligands is the same as proposed for the five-coordinated compound (II). The reaction is readily reversible, even in the solid state. Solutions gradually darken upon standing as does the solid when placed in vacuo, indicating reversion to the coordinatively unsaturated compound. This behavior is consistent with CO being *trans* to a π-acceptor ligand as is the relatively high ν(CO) frequency [4]. The position of ν(Ir—Cl) is again consistent with Cl *trans* to an oxygen donor [11b]. The intensity of the band at 538 cm^{-1} (Table 1) supports assignment of a *cis* geometry to the IrL_2 unit.



Scheme 1

Carbonyl compound III isomerizes in refluxing benzene to IV in which the phosphine ligands are *trans* (the band at 536 cm^{-1} is weak). ν(Ir—Cl) at 337 cm^{-1} and the decreased ν(C≡O) frequency, 2048 cm^{-1}, are consistent with these groups being *trans* to the diolato ligand. The isomers III and IV and Balch and Sohn's isomer Ia do not interconvert. Prolonged reflux (24—48 h) of Ia in CH_2Cl_2/C_6H_6 or $MeOH/CH_2Cl_2$ results in no change. The stability of Ia and IV is anticipated since the π-acceptor ligand CO is *trans* to a π-donor atom in each case as are the

TABLE 2

INFRARED DATA (cm^{-1}, Nujol)[a]

Compound	ν(C≡O); ν(Ir—Cl)	Compound	ν(Ir—Cl)
$IrCl(CO)L_2(o\text{-}O_2C_6Cl_4)$ (Ia)	2068vs; 305w	$\{IrClL_2(o\text{-}O_2C_6Cl_4)] \cdot C_6H_6$ (II)	321w
$IrCl(CO)L_2(o\text{-}O_2C_6Cl_4)$ (III)	2086vs; 321w	$\{IrClL_2(o\text{-}O_2C_6Cl_4)H_2O\}$ (V)[b]	314
$IrCl(CO)L_2(o\text{-}O_2C_6Cl_4)\}$ (IV)	2048vs; 337m		

[a] Bands characteristic of the diolato group occur at ca. 1530, 1258, 970, 808 and 794 cm^{-1} [13]. [b] ν(OH) 3350 cm^{-1}; δ(OH): 1670 cm^{-1}.

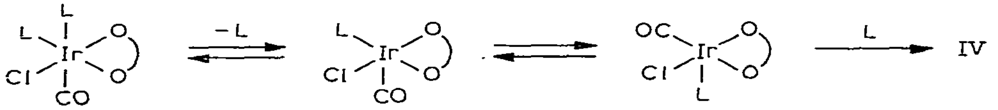
PPh_3 ligands [17]. Isomer IV is likely to be the most stable of the two since the two bulky PPh_3 ligands are mutually *trans*. The rhodium analog of II yields upon carbonylation the analog of compound IV as the only isolable product [13].

The coordinatively unsaturated compound II, adds an aquo ligand when the solid or a solution are exposed to the atmosphere. Modes due to the aquo ligand appear at 3350 cm^{-1} (ν(OH) and 1670 cm^{-1} (δ(OH)). The position of ν(Ir—Cl) (314 cm^{-1}) is consistent with Cl being *trans* to an oxygen donor. The intensity of the band at 541 cm^{-1} (Table 1) suggests that the two PPh_3 ligands are *cis*. It is assumed, in accord with a growing body of data [6,10], that the H_2O ligand adds *trans* to a PPh_3 group (ligand of highest *trans* influence).

Conclusions

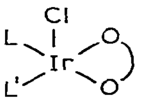
From our analysis of the infrared spectra of octahedral iridium(III) complexes containing two PPh_3 ligands it appears that Mastin's [16] criterion (developed in platinum(II) complexes) for determining whether they are mutually *cis* or *trans* can be used. Application of the method requires the careful comparison of spectra of a series of compounds to insure that bands due to other structural features of the compounds are not present in the region 530—550 cm^{-1}. The relative intensity of the pair of bands near 1580 cm^{-1} which has been suggested as a means of differentiating *cis*- and *trans*-$M(PPh_3)_2$ geometry in platinum(II) complexes [15] and used to support assignments of *trans* geometry in iridium(III) complexes is shown not to be reliable for the latter by our data.

The very high stereospecificity found for the addition of water or carbon monoxide to the five-coordinate complex II (see Scheme 1) lends further support to our previous contention and to that of Wright, Glyde and Mawby that nucleophilic addition to coordinatively unsaturated iridium(III) is kinetically directed *trans* to the ligand of highest *trans* influence. This occurs even though the isomer formed, compounds III or V, are unfavorable from the stand point of having two bulky triphenylphosphine molecules mutually *cis* and also having CO *trans* to a π-acceptor ligand in the former case. The ready isomerization of III to IV can be accounted for in same context since III can reasonably be expected to be in equilibrium with coordinatively unsaturated intermediates of the type shown (eq. 1).

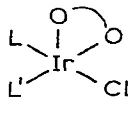


(III) (VIa) (VIb) (1)

Intermediates VIa and VIb would be expected to have similar stabilities since CO and PPh_3 are of comparable *trans* influence [11]. Assuming dissociation of only neutral ligands, formation of isomer Ia from isomers III or IV would require



(VIc)



(VId)

a five-coordinated intermediate of the type VIc or VId (L′ = CO or PPh_3) which would have a ligand of low *trans* influence (*trans* to the vacant coordination site). This is apparently not favorable and accounts for the failure of III or IV to be interconverted with Ia.

Experimental

The compounds *trans*-$[MCl(CO)(PPh_3)_2]$ (M = Ir [18] or Rh [19]), *trans*-$[IrCl(N_2)(PPh_3)_2]$ [20], $[RhCl(CO)(PPh_3)_2(o\text{-}O_2C_6Cl_4)]$ [13], $[IrCl(CO)(PPh_3)_2(o\text{-}O_2C_6Cl_4)]$ (configuration Ia) [13], $[IrBr(CO)(PPh_3)_2(TCNE)]$ [21], and $[Pt(PPh_3)_2C_2H_4]$ [22] were prepared by methods in the literature. The compound $o\text{-}O_2C_6Cl_4$ was purchased from Aldrich Chemical Company. Infrared spectra were recorded on a Perkin—Elmer Model 621 spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

$[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4)]\cdot C_6H_6$ (II). *trans*-$[IrCl(N_2)(PPh_3)_2]$ (1.0 g, 1.3 mmol), and $o\text{-}O_2C_6Cl_4$ (0.32 g, 1.3 mmol) were placed in a 25 ml, two neck flask fitted with an N_2 inlet and a sintered glass filter. The system was purged with dry N_2 and then 10 ml dry benzene was added. A color change from yellow to black, accompanied by gas evolution, occurred as the reagents mixed. After stirring for 10 min the black solid was collected in the filter by inverting the apparatus. The precipitate was washed with 7 ml cold benzene and dried in a stream of N_2 for 10 min before being transferred to a vacuum dessicator. Yield: 1.1 g, 80%, m.p. 185—191°C. Anal. (C_6H_6 solvate) Found: C, 53.44; H, 3.40; Cl, 16.47. $C_{48}H_{36}Cl_5IrO_2P_2$ calcd.: C, 53.57; H, 3.37; Cl, 16.47%.

$[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4)(H_2O)]$ (V). The complex $[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4)]\cdot C_6H_6$, (0.2 g) was dissolved in methylene chloride, (9 ml) in a beaker. As the solution is stirred exposed to the air, a yellow precipitate of the aquo complex forms. Yield: 0.18 g, m.p. 187—195°C. Found: C, 49.13; H, 3.26; Cl, 18.47. $C_{42}H_{32}Cl_5IrO_3P_2$ calcd.: C, 49.65; H, 3.17; Cl, 17.45%.

cis-$[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4)(CO)]$ (III). The complex $[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4]\cdot C_6H_6$ (0.55 g) was dissolved in methylene chloride (10 ml) in an N_2 atmosphere. Carbon monoxide was bubbled through the solution until it became yellow in color. Hexane, 25 ml, was added with continued CO flow. After 15 min the mixture was filtered yielding 0.46 g of yellow solid. The sample reversibly loses carbon monoxide in vacuo or when heated. Anal. Found: C, 50.41; H, 3.35; Cl, 17.34. $C_{43}H_{30}Cl_5IrO_3$ calcd.: C, 50.33; H, 2.95; Cl, 17.28%.

trans-$[Ir(PPh_3)_2Cl(o\text{-}O_2C_6Cl_4)(CO)]$ (IV). The complex $[IrCl(PPh_3)_2(o\text{-}O_2C_6Cl_4)]\cdot C_6H_6$ (0.5 g) in 8 ml benzene was refluxed for 30 min while carbon monoxide was bubbled through the mixture. The mixture was cooled to room temperature and hexane (20 ml) was added to complete precipitation of the product. The recovered solid was washed with hexane and dried in vacuo. Yield: 0.42 g, m.p. 254—258°C. Anal. Found: C, 50.61; H, 3.20; Cl, 17.33. $C_{43}H_{30}Cl_5IrO_3$ calcd.: C, 50.33; H, 2.95; Cl, 17.28%.

The same product was obtained in 85% yield by refluxing a solution of the above *cis* isomer III in benzene for 30 min under a CO atmosphere. Prolonged reflux (2.5 h) of the *trans* isomer results in no further change.

Attempted isomerization of $[IrCl(CO)PPh_3)_2(o\text{-}O_2C_6Cl_4)]$ (Ia). Freshly prepared samples of Ia (0.15 g) were refluxed in CH_2Cl_2/C_6H_6 and CH_2Cl_2/CH_3OH

(50/50) (4 ml) for 24 h. The mixtures were evaporated to dryness. The residues were found to be unchanged Ia by comparison of IR spectra with those of authentic samples.

[Pt(PPh$_3$)$_2$(o-O$_2$C$_6$Cl$_4$)]. Ethylenebis(triphenylphosphine)platinum(0) (0.25 g) and *o*-$O_2C_6Cl_4$ (0.08 g) in C_6H_6 (5 ml) were stirred for 5 min. The resulting yellow, crystalline precipitate was recovered and washed with ether. Yield: 0.25 g, m.p. 253—254°C. Anal. Found: C, 53.08; H, 3.43; Cl, 14.29. $C_{42}H_{30}Cl_4O_2P_2$ calcd.: C, 52.25; H, 3.13; Cl, 14.69%.

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