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Complexes of some Mixed-donor Ligands with Rh(I), Ir(I) and Ir(III)

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Reactions of the mixed bidentate ligands: 8-(diphenylarsino)quinoline (N-As), 8-(diphenylphosphino)quinoline (N-P), and 8-aminoquinoline (N-N) with the rhodium dimer, $[Rh(CO)_2Cl]_2$, were investigated. The complexes [Rh(N-As)(CO)Cl], [Rh(N-P)(CO)Cl], and $[Rh(N-N)(CO)_2]Cl$ have been isolated and characterized. Reactions of the above ligands with the iridium anion, $[Ir(CO)_2Cl_2]^-$, gave $[IrH(N-As)(CO)Cl_2]$, [Ir(N-P)(CO)Cl], and [Ir(N-N)(CO)Cl], respectively. Structures for the above complexes were assigned based on their IR and ^1H NMR spectra, analyses, electrical conductance and molecular weight measurements.

Introduction

Recently there has been interest in the coordination chemistry of unsymmetrical ligands with low-valent metal centers. Special interest was given to ligands that have an aryl phosphine or aryl arsine at one end to stabilize the metal ion in a low oxidation state, and a weakly coordinating amine (at the other end) that can be substituted by a π-acceptor species [1–4]. In a previous report [5], we have described the synthesis and chemistry of some coordination compounds of the ligands 8-(diphenylarsino)quinoline, (N-As), 8-(diphenylphosphino)quinoline, (N-P) and 8-aminoquinoline, (N-N). Reactions of the closely related ligand *o*-(diphenylphosphino)-N,N-dimethylaniline (P-NA) with some metal cations were also investigated [1, 2].

Few complexes of rhodium(I) [2,6–10] and iridium(I) [1] with mixed bidentate ligands containing nitrogen and either tertiary phosphine or arsine have been isolated. The catalytic properties of some of these complexes have also been investigated. However, none of the Rh(I) or Ir(I) complexes of the ligands (N-As), (N-P) or (N-N) have been yet reported. We now report on our efforts to isolate such coordination compounds from the reactions of the ligands with $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_2Cl_2]^-$.

Experimental

All chemicals used were of AR or GR grade and were dried as required. IR spectra were recorded on a Perkin-Elmer model 577; NMR spectra were recorded on a TA-60 Varian NMR spectrometer using $CDCl_3$ as a solvent with TMS as the internal standard. Magnetic susceptibility measurements were made at room temperature by Gouy method using $Hg[Co(CNS)_4]$ as calibrant. Conductivity measurements were made with 10^{-3} *M* nitromethane solutions using a Y.S.I. conductivity bridge model 31. The ligands (N-As) and (N-P) were prepared following published procedures [11]. 8-Aminoquinoline (TCI-GR. Japan) was purified by recrystallization from ethanol. The rhodium dimer, $[Rh(CO)_2Cl]_2$, was prepared by a simple modification of the method described by McCleverty and Wilkinson [12]. Instead of passing carbon monoxide continuously, it was allowed to pass through ethanol at half-hour intervals. Elemental analyses and molecular weight determinations (vapour pressure) were performed by E. Pascher, Microanalysis Laboratory (Bonn, W. Germany). All reactions were carried out in an atmosphere of nitrogen. The metal complexes were dried under vacuum at 50 °C.

Synthesis of the Complexes

(a) Chlorocarbonyl 8-(diphenylarsino)quinoline rhodium(I), [Rh(N-As)(CO)Cl]

To a filtered solution of $[Rh(CO)_2Cl]_2$ (0.125 mmol) in 5 ml benzene was added, a filtered solution of the ligand (N-As) (0.5 mmol) in 5 ml of benzene. Upon addition, a yellow solid separated; dry diethylether was added to complete precipitation. The solid was filtered and washed with benzene and ether.

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(b) *Chlorocarbonyl 8-(diphenylphosphino)quinoline rhodium(I), [Rh(N-P)(CO)Cl]*

This complex was prepared as (a) above by using 0.5 mmol of the ligand (N-P).

(c) *Dicarbonyl(8-aminoquinoline)rhodium(I) chloride, [Rh(N-N)(CO)$_2$] Cl*

To a filtered solution of [Rh(CO)$_2$Cl]$_2$ (0.125 mmol) in 5 ml benzene was added a filtered solution of the ligand (N-N) (0.5 mmol) in 5 ml benzene. On mixing, a dark violet solution was obtained. The solution was stirred for 15 minutes at room temperature, and then refrigerated overnight to give a dark yellow brown solid. The solid was filtered and washed with benzene and ether.

(d) *Hydridodichlorocarbonyl 8-(diphenylarsino)-quinoline iridium(III), [IrH(N-As)(CO)Cl$_2$]*

To a filtered solution of [Ir(CO)$_2$Cl$_2$]$^-$ [13] (0.5 mmol) in 10 ml of 2-methoxyethanol, a filtered solution of the ligand (N-As) (0.5 mmol) in 10 ml of ethanol was added under CO atmosphere and the mixture was refluxed for 30 minutes. When half of the solvent was removed under vacuum, a pale yellow solid was obtained. It was filtered and washed with ether.

(e) *Chlorocarbonyl 8-(diphenylphosphino)quinoline iridium(I), [Ir(N-P)(CO)Cl]*

To a filtered solution of Ph$_4$As[Ir(CO)$_2$Cl$_2$] [13] (0.5 mmol) in 15 ml of 2-methoxyethanol, a filtered solution of the ligand (N-P) (0.5 mmol) in 5 ml of a (1:1) CH$_2$Cl$_2$/C$_2$H$_5$OH mixture was added. The mixture was stirred in an ice-bath for two hours. The yellow solid that separated was filtered and wahed with ethanol and ether.

(f) *Chlorocarbonyl(8-aminoquinoline)iridium(I), [Ir(N-N)(CO)Cl]*

This complex was prepared as in (e) above. Half of the solvent was removed under vacuum. The violet solid thus obtained was filtered and washed with ether.

Results and Discussion

Analytical data for the complexes are presented in Table I; the IR data and melting points are shown in Table II.

The coordination compounds [Rh(N-P)(CO)Cl] and [Rh(N-As)(CO)Cl] have been prepared by the reaction of [Rh(CO)$_2$Cl]$_2$ with the ligands (N-P) and

TABLE I. Elemental Analyses of the Complexes.

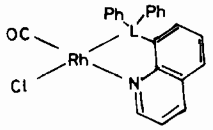
Complex	Calculated				Found			
	%C	%H	%N	%Cl	%C	%H	%N	%Cl
[Rh(N-P)(CO)Cl]	55.08	3.37	2.92	7.39	54.92	3.72	2.68	6.48
[Rh(N-As)(CO)Cl]	50.45	3.08	2.67	6.74	50.55	3.51	2.22	5.90
[Rh(N-N)(CO$_2$] Cl	39.02	2.39	8.27	10.47	37.98	2.68	8.42	10.55
[Ir(N-P)(CO)Cl]	46.44	2.84	2.46	6.23	45.51	3.08	2.73	6.20
[IrH(N-As)(CO)Cl$_2$]	40.69	2.64	2.16	10.92	41.51	2.89	1.96	10.20
[Ir(N-N)(CO)Cl]	30.03	2.02	7.00	8.87	30.39	1.98	6.44	8.17

TABLE II. Infra-red Spectra and Melting Points of the Complexes.*

Complex	CO cm^{-1}**	Rh–Cl*** cm^{-1}	Ir–Cl*** cm^{-1}	Ir–H** cm^{-1}	M.p.
[Rh(N-P)(CO)Cl]	1972(s)	296(w)	–	–	195 d
[Rh(N-As)(CO)Cl]	1974(s)	326(m) 300(w)	–	–	130 d
[Rh(N-N)(CO)$_2$] Cl	1980(s),2004(s) 2050(s),2074(s)	–	–	–	145 d
[Ir(N-P)(CO)Cl]	1962(s)	–	294(w)		230 d
[IrH(N-As)(CO)Cl$_2$]	2038(s)	–	296(m) 266(w)	2154(s)	220 d
[Ir(N-N)(CO)Cl]	2000(s),2050(s)	–	296(m.sh)	–	158 d

*s: strong, m: medium, sh: shoulder, w: weak, d: decomposition. **KBr discs. ***CsI discs.

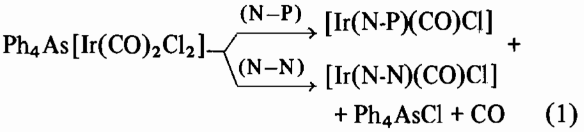
(N-As), respectively. The compounds are bright yellow, fairly stable to air and light, and are soluble in common organic solvents (acetone, chloroform, methylene chloride, *etc.*). Their IR spectra show only one strong absorption band in the terminal carbonyl region at 1972 cm^{-1} for [Rh(N-P)(CO)Cl] and 1974 cm^{-1} for [Rh(N-As)(CO)Cl]. These values indicate that CO is *trans* to the N-atom of the ligands [1]. This is consistent with the π-bonding requirements of CO and P or As donors. Placing CO in a position *trans* to P or As will have both π-acceptor ligands compete for the same filled d-orbitals of the metal atom. The Rh–Cl stretching frequencies appear at 296 and 300 cm^{-1}, respectively, corresponding to terminal Rh–Cl bonds. Molecular weight determinations support the above formulation of these complexes as monomeric (Mol. Wt. for [Rh(N-P)(CO)Cl], Found/Calc. = 1.2; and for [Rh(N-As)(CO)Cl], = 1.3) species and thus having square planar geometry, (I & II). As expected these complexes are non-electrolytes in nitromethane.



(I) L = P , [Rh(N–P)(CO)Cl]
(II) L = As , [Rh(N-As)(CO)Cl]

The reaction of the rhodium dimer with (N-P) proceeds by symmetrical breakage of the dimer, followed by substitution of one of the CO groups [14]. The substitution of the CO group seems to occur readily in the case of (N-As) and (N-P). However, in the case of (N-N), it seems that Cl$^-$ substitution occurs instead. The product obtained from the reaction of the ligand (N-N) with the rhodium dimer, [Rh(CO)$_2$Cl]$_2$, has been formulated as [Rh(N-N)(CO)$_2$]Cl [10]. Conductivity measurements for this complex in nitromethane ($\Lambda_M = 33$) coorespond to a 1:1 electrolyte. The N–H stretching frequency (3150, 3100 cm^{-1}) shows a shift of about 300 cm^{-1} towards lower frequency indicating coordination through the amine nitrogen center [5]. Unlike the complexes of (N-P) and (N-As) which contain only one carbonyl each, the IR spectrum of the [Rh(N-N)(CO)$_2$]Cl shows four carbonyl absorption bands in the terminal carbonyl region [15]. The presence of two CO's in this complex seems essential to make up for the weaker π-acceptor character of the N-donors as opposed to As and P. This behavior substantiates the importance of π-acceptor character in stabilizing the rhodium atom in its low oxidation state.

Reactions of the above-mentioned ligands with the iridium anion, [Ir(CO)$_2$Cl$_2$]$^-$, were also investigated. The compounds [Ir(N-P)(CO)Cl] and [Ir(N-N)(CO)Cl] have been prepared by the treatment of Ph$_4$As [Ir(CO)$_2$Cl$_2$] with the ligands (N-P) and (N-N), respectively (eqn. 1). The compounds are pale yellow, fairly stable to air and light, and have a square planar geometry. [Ir(N-P)(CO)Cl] is readily soluble in most organic solvents but [Ir(N-N)(CO)Cl] is only soluble in DMF and nitrobenzene.



$$\mathrm{Ph_4As[Ir(CO)_2Cl_2]} \begin{cases} \xrightarrow{(N-P)} \mathrm{[Ir(N\text{-}P)(CO)Cl]} \\ \xrightarrow{(N-N)} \mathrm{[Ir(N\text{-}N)(CO)Cl]} \end{cases} + \mathrm{Ph_4AsCl + CO} \qquad (1)$$

The IR spectrum of the complex [Ir(N-P)(CO)Cl] shows one band in the terminal carbonyl region. The value of νCO at 1962 cm^{-1} indicates that CO is *trans* to the N-atom of the ligand [1]. The Ir–Cl appears at 294 cm^{-1} corresponding to a terminal Ir–Cl bond. The complex is non-electrolyte as shown by conductivity measurements in nitromethane. The ligand (N-N) in [Ir(N-N)(CO)Cl] acts as a bidentate ligand. Coordination of the -NH$_2$ group to iridium is verified by a shift in νN–H to lower frequency (2800 cm^{-1}) [5]. The IR spectrum shows two absorption bands at 2000 and 2050 cm^{-1} [10]. These high energy values of CO stretching frequency indicate that the CO is *trans* to the heterocyclic N-atom of the ligand [1]. Conductivity measurements of this complex in nitromethane indicate that the complex is non-electrolyte.

Attempts to isolate a product from the reaction of the ligand (N-As) with Ph$_4$As [Ir(CO)$_2$Cl$_2$] were unsuccessful. However, reaction of the 2-methoxyethane solution of [Ir(CO)$_2$Cl$_2$]$^-$ with (N-As) affords a complex formulated as [IrH(N-As)(CO)Cl$_2$]. This compound is also pale yellow and soluble in common organic solvents. The presence of the hydride was confirmed by the appearance of a strong absorption band at 2154 cm^{-1} in its IR spectrum, and a high field peak (–17 ppm) in its ^{1}H NMR spectrum, in accord with reported literature values [16]. A strong absorption band appears at 2035 cm^{-1} assigned to the terminal CO group and two sharp bands at 296 and 270 cm^{-1} assigned to the terminal Ir–Cl bonds. The complex is non-electrolyte as indicated by its conductivity measurements in nitromethane. According to these data the compound seems to be an octahedral Ir(III) complex.

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