

*Anal.* Calcd for the acetonitrile adduct  $C_6H_5SO_2IrCl_2[P(C_6H_5)_3]_2 \cdot CH_3CN$ : C, 54.5; H, 3.95; N, 1.44. Found: C, 52.1; H, 3.84; N, 1.28. Pertinent ir bands ( $cm^{-1}$ ): 2322 (w), 1208 (s), 1050 (m), 588 (s), 330 (w). The addition of other Lewis bases such as diethyl sulfide, triphenylphosphine, and triphenyl phosphite was also observed to discolor the brown solutions of the sulfinatoiridium complex 4.

**Alkyl- or Aryl-Sulfur Dioxide Complexes (7).**—The sulfinato complex 4 (100 mg) was refluxed in 10 ml of benzene until the brown color faded to a pale yellow. A small amount of methanol was added to accelerate the slower reactions. A solution of 10 ml of dichloromethane and 5 ml of methanol was also found to be a suitable solvent for these reactions. The solvent was stripped under reduced pressure and the product was recrystallized from benzene-methanol or dichloromethane-methanol.

**Alkyl- or Aryldichlorocarbonylbis(triphenylphosphine)iridium(III) (8).**—A solution of the sulfur dioxide complex 7 (100 mg) in 30 ml of dichloromethane or benzene was treated with carbon monoxide at 20 psi for 24 hr. The solvent was removed under

reduced pressure and the product was recrystallized from dichloromethane-methanol.

**Kinetic Measurements.**—The rates of the rearrangement of the sulfinato complexes 4 to the sulfur dioxide complexes 7 were followed spectrophotometrically with a Cary 16 spectrometer with a thermostated cell compartment. The rates of disappearance of the sulfinato complexes  $RSO_2IrCl_2[P(C_6H_5)_3]_2$  4 were monitored by recording the absorbances at the following wavelengths for various R:  $CH_3$ , 468 nm;  $C_2H_5$ , 471 nm;  $n-C_3H_7$ , 473 nm;  $p-CH_3OC_6H_4$ , 480 nm;  $p-CH_3C_6H_4$ , 493 nm;  $C_6H_5$ , 478 nm;  $p-ClC_6H_4$ , 482 nm;  $p-O_2NC_6H_4$ , 483 nm.

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## Oxidative Addition Reactions of the Dihalodicarbonyliridate(I) Ions

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Oxidative addition reactions of the  $Ir(CO)_2X_2^-$  ions with halogens, alkyl halides, acetyl halides, mercuric halides, hydriodic acid, and tetracyanoethylene are described. Two isomers of the  $Ir(CO)_2Br_2^-$  ion have been prepared, one by oxidative addition of iodine to  $Ir(CO)_2Br_2^-$  and the other by addition of bromine to the  $Ir(CO)_2I_2^-$  ion. Infrared data for the new complexes are presented.

### Introduction

Studies on oxidative addition reactions of  $d^8$  iridium(I) have been concentrated almost exclusively on iridium-phosphine complexes.<sup>1</sup> However, in many ways the  $Ir(CO)_2X_2^-$  ions may be considered as more fundamental iridium(I) species insofar as they are the ultimate species formed in a system Ir-halide-CO in a hydroxy solvent<sup>2</sup> and are presently used as intermediates in routes to iridium(I)-phosphine complexes.<sup>3</sup> We report here the results of a study of the oxidative addition reactions of the  $Ir(CO)_2X_2^-$  ions.

### Experimental Section

Infrared spectra were obtained with a Beckman IR-12 spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer.

**Preparation of Compounds. Tetraphenylarsonium Dihalodicarbonyliridate(I).**—These compounds were prepared as described elsewhere.<sup>2</sup>

**Tetraphenylarsonium Tetrahalodicarbonyliridate(III).**—These compounds were prepared by the general method of treating the salt of the  $Ir(CO)_2X_2^-$  ion dissolved in chloroform with a slight excess of the corresponding halogen and then precipitating the iridium(III) species by addition of excess diethyl ether; yield 80–90%. *Anal.* Calcd for  $C_{26}H_{20}AsCl_4IrO_2$  ( $[(C_6H_5)_4As][Ir(CO)_2Cl_4]$ , pale yellow crystals): C, 40.36; H, 2.59; Cl, 18.34. Found: C, 39.79; H, 2.53; Cl, 18.66. Calcd for  $C_{26}H_{20}AsBr_4IrO_2$  ( $[(C_6H_5)_4As][Ir(CO)_2Br_4]$ , lemon yellow crystals): C, 32.82; H, 2.10; Br, 33.62. Found: C, 32.60; H, 1.92; Br, 33.27. Calcd for  $C_{26}H_{20}AsI_4IrO_2$  ( $[(C_6H_5)_4As][Ir(CO)_2I_4]$ , dark

brown crystals): C, 27.40; H, 1.76; I, 44.58. Found: C, 27.88; H, 1.91; I, 44.13.

**Tetraethylammonium Dibromodiododicarbonyliridate(III) (Isomer A).**— $[(C_6H_5)_4As][Ir(CO)_2Br_2]$  (0.5 g) and  $(C_2H_5)_4NBr$  (0.15 g) were dissolved in chloroform (3 ml). Iodine (0.16 g) was dissolved in chloroform (~4 ml) and added to the above solution. Orange crystals rapidly separated and were filtered off, washed with a small volume of chloroform and then diethyl ether, and air-dried; yield 0.33 g. *Anal.* Calcd for  $C_{10}H_{20}IrBr_2I_2NO_2$ : C, 15.15; H, 2.52; Br, 20.20; I, 32.05. Found: C, 15.33; H, 2.47; Br, 20.19; I, 32.07.

**Tetraethylammonium Dibromodiododicarbonyliridate(III) (Isomer B).**— $[(C_6H_5)_4As][Ir(CO)_2I_2]$  (0.5 g) and  $(C_2H_5)_4NI$  (0.13 g) were dissolved in chloroform (1.5 ml). One milliliter of a 5% solution of bromine in chloroform was added with stirring. [Note: it is necessary to use a deficiency of bromine in this experiment (~75% of molar requirement).] A dark orange solid precipitated and was filtered off, washed with a small amount of chloroform, and air-dried; yield 0.2 g. *Anal.* Calcd for  $C_{10}H_{20}IrBr_2I_2NO_2$ : C, 15.15; H, 2.52; Br, 20.20; I, 32.05. Found: C, 15.10; H, 2.44; Br, 20.70; I, 32.55.

**Tetraphenylarsonium Triiododicarbonylmethyliridate(III).**— $[(C_6H_5)_4As][Ir(CO)_2I_2]$  (0.40 g) was dissolved in methyl iodide and then the solution was evaporated to dryness. The resulting yellow solid was collected and dried *in vacuo*; yield 0.42 g; mp 123°. *Anal.* Calcd for  $C_{27}H_{23}AsI_3IrO_2$ : C, 31.54; H, 2.24; I, 37.06. Found: C, 32.20; H, 2.26; I, 36.78.

**Tetraphenylarsonium Dichlorodiododicarbonylmethyliridate(III).**— $[(C_6H_5)_4As][Ir(CO)_2Cl_2]$  (0.5 g) was dissolved in methyl iodide and then the solution was evaporated to dryness. The resulting solid was collected and dried in air; yield 0.53 g. *Anal.* Calcd for  $C_{27}H_{23}AsCl_2I_2IrO_2$ : C, 38.39; H, 2.73; Cl, 8.40; I, 15.04. Found: C, 38.19; H, 2.64; Cl, 8.68; I, 15.51.

**Tetraphenylarsonium Trichlorodicarbonylallyliridate(III).**— $[(C_6H_5)_4As][Ir(CO)_2Cl_2]$  (0.5 g) was dissolved in chloroform (5 ml) and excess allyl chloride (~1 ml) was added. After 2 min excess diethyl ether was added to the mixture. The white precipitate which formed was separated and recrystallized from

(1) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968), and references therein.

(2) D. Forster, *Inorg. Nucl. Chem. Lett.*, **5**, 433 (1969).

(3) J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc. A*, 604 (1967).

chloroform-diethyl ether; yield 0.35 g. *Anal.* Calcd for  $C_{29}H_{25}AsCl_3IrO_2$ : C, 44.70; H, 3.21; Cl, 13.66. Found: C, 45.08; H, 3.46; Cl, 14.02.

**Tetraphenylarsonium Trichlorodicarbonylacetyliridate(III).**— $[(C_6H_5)_4As][Ir(CO)_2Cl_2]$  (0.5 g) was dissolved in chloroform (~5 ml) and acetyl chloride (1 ml) was added. After 2 min excess diethyl ether was added to the mixture and the pale yellow complex precipitated. The solid was filtered, washed with diethyl ether, and dried *in vacuo*; yield 0.45 g. *Anal.* Calcd for  $C_{28}H_{23}AsIrCl_3O_3$ : C, 43.05; H, 2.95; Cl, 13.63. Found: C, 43.45; H, 3.03; Cl, 13.70.

**Tetraphenylarsonium Tribromodicarbonylacetyliridate(III).**—This compound was prepared as described above for the analogous chloro complex. *Anal.* Calcd for  $C_{28}H_{23}AsIrBr_3O_3$ : C, 36.76; H, 2.52; Br, 26.23. Found: C, 36.46; H, 2.60; Br, 26.66.

**Tetraphenylarsonium Trichlorodicarbonyl(chloromercury)iridate(III).**— $[(C_6H_5)_4As][Ir(CO)_2Cl_2]$  (0.5 g) was dissolved in chloroform (~3 ml) and added to a solution of mercuric chloride (0.2 g) in chloroform (20 ml) whereupon a dark brown precipitate formed. Diethyl ether (50 ml) was added to the mixture and the solids formed were filtered off and purified by dissolving in chloroform (30 ml) containing mercuric chloride (0.1 g), filtering, and precipitating the complex as a yellow powder by addition of excess diethyl ether; yield 0.2 g. *Anal.* Calcd for  $C_{26}H_{20}AsHgIrCl_4O_2$ : C, 32.04; H, 2.05; Cl, 14.59. Found: C, 32.50; H, 2.16; Cl, 15.13.

**Tetraphenylarsonium Tribromodicarbonyl(bromomercury)iridate(III).**—This compound was prepared as a yellow powder by an analogous method to that of the chloro compound above. *Anal.* Calcd for  $C_{26}H_{20}AsHgIrBr_4O_2$ : C, 27.10; H, 1.74; Br, 27.76. Found: C, 27.73; H, 1.66; Br, 27.51.

## Results and Discussion

Infrared data for the new compounds are presented in Table I.

TABLE I  
INFRARED SPECTRA OF IRIIDIUM(III)-DICARBONYL SPECIES

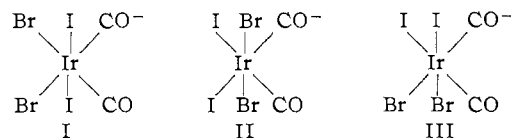
| Compound                               | Medium     | $\nu(CO),^a$ $cm^{-1}$      |
|--|------------|-----------------------------|
| $[(C_6H_5)_4As][Ir(CO)_2Cl_4]$         | $CH_3NO_2$ | 2143, 2094                  |
| $[(C_6H_5)_4As][Ir(CO)_2Br_4]$         | $CH_3NO_2$ | 2133, 2087                  |
| $[(C_6H_5)_4As][Ir(CO)_2I_4]$          | $CH_3NO_2$ | 2115, 2070                  |
| $[(C_2H_5)_4N][Ir(CO)_2Br_2I_2]$ A     | $CH_3NO_2$ | 2126, 2079                  |
| $[(C_2H_5)_4N][Ir(CO)_2Br_2I_2]$ B     | $CH_3NO_2$ | 2120, 2070                  |
| $[(C_6H_5)_4As][Ir(CO)_2I_3CH_3]$      | $CH_3NO_2$ | 2102, 2049                  |
| $[(C_6H_5)_4As][Ir(CO)_2Cl_2I_2CH_3]$  | $CH_3NO_2$ | 2113, 2057                  |
| $[(C_6H_5)_4As][Ir(CO)_2Cl_3(CH_3CO)]$ | $CHCl_3$   | 2126, 2069,<br>1688 w, 1668 |
| $[(C_6H_5)_4As][Ir(CO)_2Br_3(CH_3CO)]$ | $CHCl_3$   | 2120, 2066,<br>1687 w, 1667 |
| $[(C_6H_5)_4As][Ir(CO)_2Cl_3(allyl)]$  | $CH_3NO_2$ | 2116, 2059                  |
| $[(C_6H_5)_4As][Ir(CO)_2Cl_3(HgCl)]$   | $CHCl_3$   | 2117, 2066                  |
| $[(C_6H_5)_4As][Ir(CO)_2Br_3(HgBr)]$   | $CHCl_3$   | 2110, 2060                  |
| $[(C_6H_5)_4As][Ir(CO)_2Cl_2] + TCNE$  | $CH_3NO_2$ | 2127, 2081                  |
| $[(C_6H_5)_4As][Ir(CO)_2Br_2] + TCNE$  | $CH_3NO_2$ | 2122, 2078                  |
| $[(C_6H_5)_4As][Ir(CO)_2I_2] + TCNE$   | $CH_3NO_2$ | 2119, 2076                  |

<sup>a</sup> All bands are strong unless noted otherwise.

**Reaction with Halogens.**—The  $Ir(CO)_2X_2^-$  ions oxidatively add halogens very rapidly at room temperature in alcohols, halocarbons, and acetonitrile to give the *cis*- $Ir(CO)_2X_4^-$  ions. The product of the reaction does not depend upon the solvent unlike the corresponding rhodium system where monocarbonylrhodium(III) species are the product of oxidative addition of halogens to  $Rh(CO)_2X_2^-$  ions in alcohols and the *cis*- $Rh(CO)_2X_4^-$  ions in halocarbon solvents such as chloroform. The  $Ir(CO)_2X_4^-$  ions are more stable than their rhodium analogs and only lose a carbonyl on heating at 150° in nitrobenzene.<sup>4</sup>

Two isomers of the anion  $Ir(CO)_2Br_2I_2^-$  have been prepared, one by addition of iodine to  $Ir(CO)_2Br_2^-$  (isomer A) and the other by addition of bromine to

$Ir(CO)_2I_2^-$  (isomer B). Both contain *cis* carbonyls as evidenced by the observation of two carbonyl stretching bands of almost equal intensity, and thus, there are three possible structures.



In view of the trend in CO stretching frequencies of carbonyls *trans* to halides in iridium(III)-halocarbonyl complexes which follows the order  $Cl > Br > I$  (see Table I), we expect isomer I to have the highest CO frequencies. Now the isomer obtained by addition of iodine to  $Ir(CO)_2Br_2^-$  has higher CO frequencies than the other isomer isolated (see Table I). Thus, the isomer with the higher frequencies could be structure I or III. However, there is another route to the isomer with the higher CO frequencies which strongly indicates that I is the correct structure. We have been studying halide exchange and preferences in iridium(I) and iridium(III) dicarbonyl complexes,<sup>5</sup> and we note that in  $Ir(CO)_2X_4^-$  ions the halides *trans* to carbonyls exchange rapidly with other halides at room temperature and the lighter halides are preferred in these positions. Thus, if the  $IrI_4(CO)_2^-$  ion is treated with bromide ion in a nonaqueous solvent, new carbonyl stretching bands at 2126 and 2078  $cm^{-1}$  are observed; *i.e.*, the same isomer is formed as obtained by oxidative addition of iodine to the  $Ir(CO)_2Br_2^-$  ion. This strongly suggests that isomer I is formed by *trans* addition of iodine to  $Ir(CO)_2Br_2^-$ . The other isomer could therefore be II or III. It seems logical to assume that it is isomer II formed by *trans* oxidative addition of bromine to  $Ir(CO)_2I_2^-$  but definitive proof for this is lacking at this time.

Isomer I is the most stable isomer of the two prepared, since on heating the other isomer in nitromethane at 100° for 2 hr it rearranges to I.

**Reaction with Alkyl Halides.**—The  $Ir(CO)_2I_2^-$  ion undergoes a rapid reaction with methyl iodide at 25° (complete within minutes), giving the  $Ir(CO)_2I_3CH_3^-$  ion. This contrasts markedly with the corresponding rhodium system<sup>6</sup> where the methylrhodium species, presumed to form initially by interaction of methyl iodide with  $Rh(CO)_2I_2^-$ , rapidly isomerizes to a dimeric acetyl species. The  $Ir(CO)_2I_3CH_3^-$  ion, in the form of its tetraphenylarsonium salt, shows no tendency to isomerize to an acetyl species up to 150°.

Methyl iodide reacts with the  $Ir(CO)_2Cl_2^-$  ion to give the  $Ir(CO)_2Cl_2ICH_3^-$  ion (stereochemistry unknown at this time) without evidence of halide exchange. By contrast methyl iodide reacts with  $Rh(CO)_2X_2^-$  ( $X = Br$  or  $Cl$ ) with concurrent halide exchange and the final product is an essentially pure acetyltriiodorhodium(III) species.<sup>6</sup>

Allyl chloride reacts rapidly with  $Ir(CO)_2Cl_2^-$  giving the  $Ir(CO)_2Cl_3(allyl)^-$  ion. The nmr of this latter species indicates that the allyl is  $\sigma$  bonded and nonlabile at least up to 80°. By contrast the  $Co(CN)_5(allyl)^{3-}$  ion, although a  $d^6$  octahedral complex (as is the iridium

(5) D. Forster, to be submitted for publication.

(6) D. Forster, to be submitted for publication.

compound), displays an anomalous nmr because of a  $\sigma$ - $\pi$  transformation in the allyl group<sup>7</sup> induced by cyanide lability.

**Reaction with Hydrogen Halides.**—Whereas iridium(I)-phosphine complexes readily add hydrogen chloride to give iridium(III) hydrides, the  $\text{Ir}(\text{CO})_2\text{Cl}_2^-$  ion does not react with dry HCl at room temperature. Hydriodic acid in excess will react with  $\text{Ir}(\text{CO})_2\text{X}_2^-$  ions to give  $\text{Ir}(\text{CO})_2\text{I}_4^-$  and hydrogen. When a solution of  $[(\text{C}_6\text{H}_5)_4\text{As}][\text{Ir}(\text{CO})_2\text{I}_2]$  in nitromethane is treated with an equimolar quantity of concentrated aqueous hydriodic acid, a new species is formed with strong carbonyl stretching bands at 2107 and 2056  $\text{cm}^{-1}$  and a weak band at 2160  $\text{cm}^{-1}$ . These bands may be those of the  $\text{HIr}(\text{CO})_2\text{I}_3^-$  ion, but attempts to isolate this ion as a solid salt were unsuccessful.

**Reactions with Acyl Halides.**—Acetyl halides add rapidly to  $\text{Ir}(\text{CO})_2\text{X}_2^-$  ions at room temperature giving  $\text{Ir}(\text{CO})_2\text{X}_3(\text{CH}_3\text{CO})^-$  ions. This is in marked contrast

with the analogous rhodium system where acyl halides could not be added.

**Reactions of Olefins.**—Simple olefins do not react with  $\text{Ir}(\text{CO})_2\text{X}_2^-$  ions at temperatures in the range 20–100°. However, tetracyanoethylene reacts essentially immediately with  $\text{Ir}(\text{CO})_2\text{X}_2^-$  ions at 25° giving new species which we have not been able to isolate as solids but appear to be  $\text{Ir}(\text{CO})_2\text{X}_2(\text{TCNE})^-$ . These species exhibit two CO stretching frequencies in positions regarded as that of Ir(III) (see Table I). Again, a difference is observed between the corresponding iridium and rhodium systems. In reactions of TCNE with  $\text{Rh}(\text{CO})_2\text{X}_2^-$  ions, addition is accompanied by loss of a carbonyl group.<sup>6</sup>

**Reactions with Mercuric Halides.**—Mercuric halides react essentially instantaneously with  $\text{Ir}(\text{CO})_2\text{X}_2^-$  ions at room temperature giving  $\text{Ir}(\text{CO})_2\text{X}_3(\text{HgX})^-$  ions.

**Acknowledgment.**—The author wishes to thank Mr. G. V. Johnson for recording some of the infrared spectra.

(7) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **8**, 421 (1965).

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## Copper(II) Complexes with 13-Membered Macrocyclic Ligands Derived from Triethylenetetramine and Acetylacetone

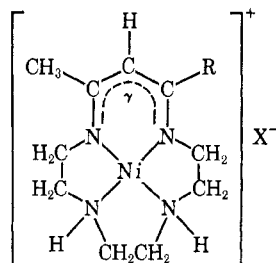
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Seven new macrocyclic copper(II) complexes  $\text{Cu}(\text{AT})\text{X}$ , where  $\text{X}^-$  is  $\text{NO}_3^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ , and  $\text{PF}_6^-$ , and  $\text{Cu}(\text{ATH})\text{X}_2$ , where  $\text{X}^-$  is  $\text{I}^-$  and  $\text{PF}_6^-$ , have been prepared and characterized. These compounds contain the uninegative ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene (AT) and the neutral ligand 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene (ATH) which are formed in the presence of copper(II) ions. The  $\text{Cu}(\text{AT})\text{X}$  and  $\text{Cu}(\text{ATH})\text{X}_2$  complexes can be interconverted in solution by reversible protonation of the coordinated ligand ( $K_a = 10^{-9}$ ). The relative acidity of the coordinated ligand in  $\text{Cu}(\text{ATH})\text{X}_2$  is 1000-fold less than in the analogous nickel(II) complex.

### Introduction

Recently we reported the synthesis of macrocyclic nickel(II) complexes (I), abbreviated  $\text{Ni}(\text{AT})\text{X}$  and  $\text{Ni}(\text{TAT})\text{X}$ ,<sup>1</sup> via condensation of triethylenetetramine (trien) and the required  $\beta$ -diketone in the presence of



I

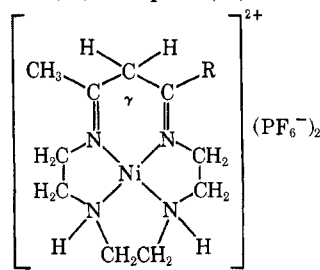
TAT, R =  $\text{CF}_3$

AT, R =  $\text{CH}_3$

$\text{X}^- = \text{I}^-, \text{Br}^-, \text{SCN}^-, \text{NO}_3^-, \text{PF}_6^-, \text{BF}_4^-, \text{and } \text{ClO}_4^-$

the metal ion.<sup>2</sup> The identity of the 13-membered macrocyclic ligand, which contains a partially delocalized planar six-membered chelate ring, has since been confirmed by a single-crystal X-ray structure determination on  $\text{Ni}(\text{AT})\text{ClO}_4$ .<sup>3</sup>

Further investigations of the  $\text{Ni}(\text{AT})^+$  system have shown that, in acidic solutions, protonation of the coordinated ligand occurs at the methine ( $\gamma$ ) carbon atom in I, and a nickel(II) complex (II) containing the neu-



II

(2) (a) S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, **92**, 215 (1970); (b) *Inorg. Chem.*, **9**, 1131 (1970).

(3) M. F. Richardson and R. E. Sievers, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.

(1) TAT is 11-methyl-13-trifluoromethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene, and AT is 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-diene.