

Contribution from the Department of Chemistry,  
Northwestern University, Evanston, Illinois 60201**Synthesis of Novel Methyliridium(III) Compounds from Substitution-Labile  
IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(X), X = SO<sub>3</sub>F or SO<sub>3</sub>CF<sub>3</sub>**

D. STROPE and D. F. SHRIVER\*

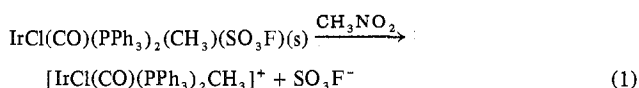
Received April 22, 1974

AIC402649

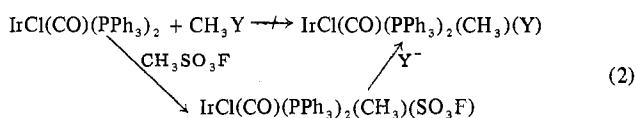
Addition of CH<sub>3</sub>SO<sub>3</sub>F or CH<sub>3</sub>SO<sub>3</sub>CF<sub>3</sub> to IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> results in the highly labile oxidative addition product IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(X) (X = SO<sub>3</sub>F or SO<sub>3</sub>CF<sub>3</sub>). Substitution of various anions for SO<sub>3</sub>F<sup>-</sup> or SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> provides a convenient route to a series of Ir(III) complexes which are inaccessible *via* direct oxidative addition. The iridium(III) complexes prepared by this route are of type 4 with X = F, Cl, Br, I, NCS, NCO, N<sub>3</sub>, ONO, NO<sub>3</sub>, CH<sub>3</sub>COO, S<sub>2</sub>O<sub>2</sub>C<sub>7</sub>H<sub>7</sub>, (NC)<sub>2</sub>Pt(CN)<sub>2</sub>, and NCC(CN)<sub>2</sub>. Vibrational and nmr spectroscopies establish that X is *trans* to CH<sub>3</sub> and triphenylphosphines are mutually *trans*. In several cases the mode of linkage to the metal (indicated above by the italic element) was determined.

**Introduction**

Reactions of the strong carbo cation reagents CH<sub>3</sub>SO<sub>3</sub>F and CH<sub>3</sub>SO<sub>3</sub>CF<sub>3</sub> with transition metal-organometallic complexes yield interesting new metal-alkyl compounds.<sup>1-3</sup> Among the products which we have reported is IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(SO<sub>3</sub>F), which is a 1:1 electrolyte in polar organic solvents owing to the ready dissociation of the SO<sub>3</sub>F<sup>-</sup> ion (eq 1). This facile dissociation results in high lability of



the methyl fluorosulfate complex and therefore provides a route to new compounds which cannot be prepared by direct oxidative addition (eq 2). The synthetic utility of this new



reaction sequence is illustrated in the present paper and structures of the products are elucidated.

**Results and Discussion**

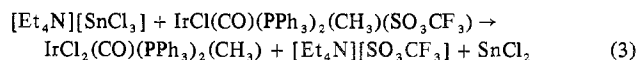
**Substitution Reactions.** With an excess of CH<sub>3</sub>SO<sub>3</sub>F or CH<sub>3</sub>SO<sub>3</sub>CF<sub>3</sub> a solution of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> decolorizes and a white solid, IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(X) (X<sup>-</sup> = SO<sub>3</sub>F<sup>-</sup>, SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>), may be precipitated from solution. In DCCl<sub>3</sub> solution the <sup>1</sup>H nmr of the methyl fluorosulfate derivative exhibits a triplet for the methyl group (τ 8.93, *J*<sub>P-H</sub> = 7 Hz, area 3) and an unresolved phenyl proton resonance (τ 2.68, area 33). The high ν<sub>CO</sub> (2064 cm<sup>-1</sup>, Nujol mull) and the molecular weight in HCCl<sub>3</sub>, 884, indicate either a six-coordinate, substitution-inert molecular species (calcd mol wt 894), similar to the usual oxidative addition products, or an ion pair. In the polar solvent nitromethane this compound exhibits a conductance of 71 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, characteristic of a 1:1 electrolyte, while retaining its high ν<sub>CO</sub> at 2062 cm<sup>-1</sup>. High conductivity and high ν<sub>CO</sub>, 2062 cm<sup>-1</sup>, are also observed for a solution in acetonitrile. The unsolvated IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(SO<sub>3</sub>F) can be recovered from acetonitrile indicating that, if the solvent is coordinated to the Ir(III) in solution, it is only weakly held. No deliberate at-

tempt was made to isolate the unstable CH<sub>3</sub>CN-containing cation which may exist in acetonitrile solution.

This dissociation of the SO<sub>3</sub>F<sup>-</sup> and SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> in polar solvents, which presumably occurs because of the high lability of these groups, leaves a readily accessible site for coordination of more strongly coordinating anions. Accordingly, a variety of anions were added to CH<sub>3</sub>NO<sub>2</sub> or CH<sub>3</sub>CN solutions of the IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(X) (X<sup>-</sup> = SO<sub>3</sub>F<sup>-</sup>, SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>) to precipitate the white or off-white six-coordinate substitution products in high yield (eq 2). In general, the reactions with the SO<sub>3</sub>CF<sub>3</sub><sup>-</sup> complex were found to be more facile. The substitution reaction is quite general in scope allowing the preparation of the F, Cl, Br, I, NCS, NCO, N<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub>, S<sub>2</sub>O<sub>2</sub>C<sub>7</sub>H<sub>7</sub> (thiotosylate), CH<sub>3</sub>COO, Pt(CN)<sub>4</sub>, and C(CN)<sub>3</sub> ligated Ir(III) complexes. These complexes were characterized by elemental analyses and decomposition points (Table I), as well as <sup>1</sup>H nmr and infrared spectroscopy (Table II).

All of these products display high ν<sub>CO</sub> characteristic of Ir(III) species (Table II) and show solubilities characteristic of nonionic complexes. Several of these compounds exhibit two bands for the ν<sub>CO</sub> when run as solid mulls. However, solution spectra show only one band with removal of the solvent again giving two bands, which presumably arise from either correlation field coupling of the CO stretches in the solid or from the existence of the complex in nonequivalent sites in the crystal.

Several other anions resulted in decomposition reactions or oxidation under the conditions used here. For example, the reaction of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(SO<sub>3</sub>CF<sub>3</sub>) with an aqueous solution of NaCN resulted in yellow-brown intractable products, and addition of BH<sub>4</sub><sup>-</sup> or BH<sub>3</sub>CN<sup>-</sup> to the cationic complex resulted in yellow or brown oils. These reactions were not pursued further. Interesting ligand abstraction reactions occur with SnCl<sub>3</sub><sup>-</sup>, PbBr<sub>3</sub><sup>-</sup>, and W(CO)<sub>5</sub>Cl<sup>-</sup> as the anions. A halide is removed from each anion to give the previously known dihalo complexes (eq 3).



Addition of an aqueous solution of LiOH to IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(SO<sub>3</sub>F) in nitromethane results in a rapid change from colorless to yellow and then dark blue. Judging from its color this product is Ir(OH)<sub>4</sub>. There is no sign of this product in any of the other reactions involving aqueous solutions of the anionic ligand. Mixing of Na[Mn(CO)<sub>5</sub>] and IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)(SO<sub>3</sub>F) in tetrahydrofuran under air-free conditions results in oxidation of the Mn(CO)<sub>5</sub><sup>-</sup> to Mn<sub>2</sub>(CO)<sub>10</sub> plus other uncharacterized products.

(1) D. Strope and D. F. Shriver, *J. Amer. Chem. Soc.*, **95**, 8197 (1973).

(2) C. Eaborn, N. Farrell, J. L. Murphy, and A. Pidcock, *J. Organometal. Chem.*, **55**, C68 (1973).

(3) J. L. Peterson, T. E. Nappier, Jr., and D. E. Meek, *J. Amer. Chem. Soc.*, **95**, 8195 (1973).

**Table I.** Analytical Data and Decomposition Points for the  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{X})$  Complexes

| X  | % C   |       | % N   |       | % H   |       | Dec pt,<br>°C    |
|--|-------|-------|-------|-------|-------|-------|------------------|
|  | Calcd | Found | Calcd | Found | Calcd | Found |                  |
| $\text{SO}_3\text{F}$                      | 51.05 | 51.24 | 0     | 0     | 3.69  | 3.95  | 202-205          |
| $\text{SO}_3\text{CF}_3$                   | 49.61 | 48.88 | 0     | 0     | 3.52  | 3.36  | 224-227          |
| $\text{S}_2\text{O}_2\text{C}_7\text{H}_7$ | 54.98 | 54.56 | 0     | 0     | 4.07  | 4.11  | 130-140          |
| F  | 56.01 | 55.23 | 0     | 0     | 4.06  | 4.90  | 283-288          |
| Cl   | 54.94 | 54.54 | 0     | 0     | 3.97  | 4.19  | 290-293          |
| Br   | 52.11 | 52.01 | 0     | 0     | 3.78  | 3.89  | 276 <sup>a</sup> |
| $\text{NO}_3$                              | 53.21 | 52.69 | 1.63  | 1.64  | 3.85  | 4.06  | 212-214          |
| $\text{CH}_3\text{COO}$                    | 56.20 | 55.88 | 0     | 0     | 4.22  | 4.34  | 203-207          |
| NCS  | 54.89 | 53.84 | 1.64  | 1.83  | 3.89  | 4.06  | 223-228          |
| NCO  | 55.95 | 55.59 | 1.67  | 1.43  | 3.97  | 4.17  | 244 <sup>a</sup> |
| $\text{N}_3$                               | 54.48 | 54.47 | 5.02  | 4.49  | 3.92  | 4.07  | 225 <sup>a</sup> |
| $\text{NO}_2$                              | 54.22 | 52.91 | 1.67  | 1.61  | 3.92  | 4.35  | 195 <sup>a</sup> |
| $\text{C}(\text{CN})_3$                    | 56.95 | 56.82 | 4.75  | 4.02  | 3.73  | 3.48  | 208-210          |
| $\text{Pt}(\text{CN})_4$ <sup>b</sup>      | 50.82 | 50.69 | 2.95  | 2.91  | 3.49  | 3.75  | 210              |

<sup>a</sup> Temperature at which gradual decomposition started. <sup>b</sup> Molecular formula  $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)]_2\text{X}$ . The observed molecular weight in  $\text{CHCl}_3$  is 2300, calcd 1889. Owing to low solubility, this determination was performed on a very dilute solution and therefore is of low accuracy.

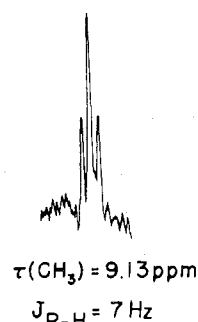
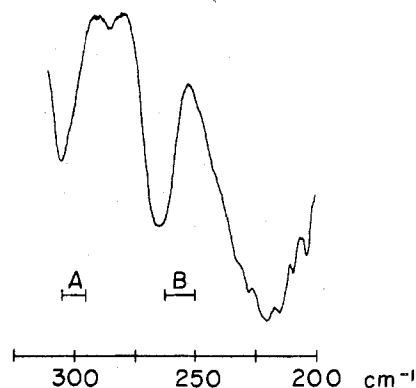
**Table II.** Mid- and Far-Infrared ( $\text{cm}^{-1}$ ) and  $^1\text{H}$  Nmr (ppm) Data for  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{X})$  Complexes

| X  | $\nu_{\text{C}\equiv\text{O}}$ |                   | $\nu_{\text{Ir-Cl}}^a$ | $\tau_{\text{CH}_3}^e$ |
|--|--------------------------------|-------------------|------------------------|------------------------|
|  | Solid <sup>a</sup>             | Soln <sup>c</sup> |                        |                        |
| $\text{SO}_3\text{F}$                      | 2064                           | 2062 <sup>b</sup> | 309                    | 8.93                   |
| $\text{SO}_3\text{CF}_3$                   | 2065                           | 2056              | 307                    | 8.73                   |
| $\text{S}_2\text{O}_2\text{C}_7\text{H}_7$ | 2045                           | 2052              | 305                    | 8.73                   |
| F  | 2051, 2027                     | 2043              | 300                    | 9.43                   |
| Cl   | 2048, 2025                     | 2039              | 304, 264               | 9.44                   |
| Br   | 2051, 2033                     | 2044              | 303                    | 9.16                   |
| I  | 2050                           | 2043              | 299 <sup>d</sup>       |                        |
| $\text{CH}_3\text{COO}$                    | 2025                           | 2040              | 304                    | 9.23                   |
| $\text{NO}_3$                              | 2056                           | 2047              | 308                    | 9.13                   |
| NCS  | 2054                           | 2047              | 303                    | 9.46                   |
| NCO  | 2040                           | 2041              | 298                    | 9.53                   |
| $\text{N}_3$                               | 2053                           | 2051              | 300                    | 9.36                   |
| $\text{NO}_2$                              | 2050, 2032                     | 2042              | 303                    | 9.16                   |
| $\text{C}(\text{CN})_3$                    | 2055, 2012                     | 2055              | 304                    | 9.13                   |
| $\text{Pt}(\text{CN})_4$ <sup>f</sup>      | 2056                           | 2054              | 303                    | 9.54                   |

<sup>a</sup> Nujol mull. <sup>b</sup>  $\text{CH}_3\text{NO}_2$  solution. <sup>c</sup>  $\text{CH}_2\text{Cl}_2$  solution. <sup>d</sup> W. R. Muir, Ph.D. Thesis, Northwestern University. <sup>e</sup>  $\text{CDCl}_3$  solution. <sup>f</sup> The molecular formula of this complex is  $(\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3))_2\text{Pt}(\text{CN})_4$ .

**Stereochemistry.** All of the complexes, except one, formed from reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$  and anions were found to be soluble enough for the convenient determination of  $^1\text{H}$  nmr spectra, the exception being the well-known  $\text{CH}_3\text{I}$  addition product. The room-temperature spectra of  $\text{CDCl}_3$  solutions of all of the other complexes (Table II) show a triplet for the methyl group (Figure 1) indicating that the methyl group is cis to two equivalent phosphines which are trans to each other. The phenyl protons of all of these species show broad, partially resolved resonances around  $\tau$  2.5 with integrated areas in the range of 10-11 times that of the methyl resonances, as is expected for monomethylbis(triphenylphosphine)iridium(III) complexes. Methyl resonances for the  $\text{S}_2\text{O}_2\text{C}_7\text{H}_7^-$ ,  $\text{SO}_3\text{F}^-$ , and  $\text{SO}_3\text{CF}_3^-$  compounds occur at significantly lower fields than for any of the other compounds.

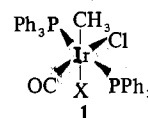
Remaining details of the stereochemistry around the metal can be established by determination of the group trans to CO via far-infrared spectroscopy. Jenkins and Shaw<sup>4</sup> have shown that the absorption frequency of the metal-halogen stretch in this type of complex is dependent on the nature

(4) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 6789 (1965).**Figure 1.** Nmr spectrum in the methyl region for  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{C}(\text{CN})_3)$ .**Figure 2.** Far-infrared spectrum for  $\text{IrCl}_2(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)$ . Absorptions in the A region, which represent Cl trans to CO, were seen for all compounds reported here. The B region is diagnostic of Cl trans to alkyl and in the present work was observed only for the dichloro complex.

of the group trans to the halogen. A chloro group trans to an alkyl group has its Ir-Cl stretch from 250 to 260  $\text{cm}^{-1}$  while this band is from 270 to 275  $\text{cm}^{-1}$  in complexes with the chloro group trans to a phosphine.<sup>5</sup> Also, a  $\text{Cl}^-$  trans to CO absorbs at 310-315  $\text{cm}^{-1}$  in planar complexes and at 295-305  $\text{cm}^{-1}$  in octahedral complexes.

In all of the compound reported here there is a band assignable as  $\nu_{\text{Ir-Cl}}$  between 298 and 309  $\text{cm}^{-1}$  (Table II), thereby indicating a  $\text{Cl}^-$  trans to CO in all of the complexes (Figure 2). Interestingly, the  $\nu_{\text{Ir-Cl}}$  of the complexes containing the poorly coordinating anions  $\text{NO}_3^-$ ,  $\text{SO}_3\text{F}^-$ , and  $\text{SO}_3\text{CF}_3^-$  are intermediate between those shown by the square-planar and octahedral complexes (Table II). Presumably, these anions are less tightly bound, thereby strengthening the Ir-Cl bond. As expected, the dichloro complex shows a second band at 264  $\text{cm}^{-1}$  for the  $\text{Cl}^-$  trans to the  $\text{CH}_3$ .

These results, when combined with those from the  $^1\text{H}$  nmr spectra, establish the  $\text{CH}_3\text{-X}$  configuration as trans in all of the six-coordinate complexes mentioned here. Two types of experiments were done to confirm that the complexes measured by solution  $^1\text{H}$  nmr and solid far-infrared spectroscopy were not isomers whose configuration depended on environment. First, the same isomeric form was recovered from solution after successive dissolutions. Second, far-infrared spectra obtained from  $\text{CHCl}_3$  solutions of the  $\text{CH}_3\text{-COO}^-$  and  $\text{NO}_2^-$  complexes exhibited a  $\nu_{\text{Ir-Cl}}$  in the region appropriate for  $\text{Cl}^-$  trans to CO in an octahedral complex 1.

(5) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969).

It then appears that, at room temperature and in the solvents used here, these complexes do not undergo any observable isomerization reactions and retain the trans arrangement for the  $\text{CH}_3$  and X groups in solution as well as in the solid state.

**Linkage of Polyatomic Ligands.** Reed and Roper<sup>6</sup> and DeStefano and Burmeister<sup>7</sup> have reported the preparation of Ir(I) complexes having X trans to CO. It was found that ambident X ligands containing both "hard" and "soft" bonding sites were generally bonded to Ir(I) through the hard site. This was attributed to the  $\pi$  donor abilities of "hard" ligands, which stabilize both CO and anion bonding.

The  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{NCS})$  complex appears to follow the pattern found for the Ir(I) analogs, with the  $\text{NCS}^-$  group coordinated through the "hard" N atom. This complex shows  $\nu_{\text{CN}}$  at  $2108\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  solution—positions which are marginal between the CN frequencies expected for either isomer.<sup>8,9</sup> Pecile<sup>10</sup> has shown the integrated intensity of the CN stretch to be quite diagnostic of the type of attachment. Meaningful integrated intensities could not be obtained, however, owing to heavy overlap between the  $\nu_{\text{CN}}$  and the  $\nu_{\text{CO}}$  at  $2047\text{ cm}^{-1}$ . The CS stretch has also been found to be a sensitive measure of the type of bonding showing  $\nu_{\text{CS}}$  from  $780$  to  $860\text{ cm}^{-1}$  for the N-bonded isomer and from  $690$  to  $720\text{ cm}^{-1}$  for the S-bonded isomer. A weak band possibly assignable as  $\nu_{\text{CS}}$  for the N-bonded isomer of this complex is observed at  $825\text{ cm}^{-1}$  while the region from  $680$  to  $720\text{ cm}^{-1}$  is obscured by phosphine bands which are little changed in the  $\text{NCS}^-$  complex from those in the other complexes. There is some precedent for bonding through the "hard" N end of the ligand in Ir(III) chemistry since the N-bonded isomer is the predominant form for  $[\text{Ir}(\text{NH}_3)_5(\text{NCS})^{2+}]$ .<sup>11</sup>

Four types of bonding are possible for the  $\text{NO}_2^-$  group: N bonded, nitro; O bonded, nitrito; O bonded, bidentate; O bonded, bridging. The latter possibility can be dismissed owing to the analytical data which show six ligands per Ir(III), leaving no coordination sites open for  $\text{NO}_2$  bridges. The complex discussed here is the O-bonded nitrito isomer as shown by a new strong band at  $1405\text{ cm}^{-1}$  with a medium shoulder at  $1395\text{ cm}^{-1}$  and another new strong band at  $1099\text{ cm}^{-1}$ . These frequencies agree with those previously found for the terminal and bridging NO stretch of O-bonded (nitrito) complexes. By contrast the lower frequency NO stretch is found near  $1300\text{ cm}^{-1}$  in the N-bonded (nitro) complexes.<sup>12,13</sup> Basolo and Hammaker<sup>14,15</sup> have prepared the  $[\text{Ir}(\text{NH}_3)_5\text{ONO}]^{2+}$  and  $[\text{Ir}(\text{NH}_3)_5\text{NO}_2]^{2+}$  isomers both of which contain Ir(III). In their experiments the nitrito isomer eventually converted to the nitro isomer. However, the nitrito group in  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{ONO})$  does not isomerize at room temperature even after several days of stirring in solution.

(6) C. A. Reed and W. R. Roper, *J. Chem. Soc., Dalton Trans.*, 1370 (1973).

(7) N. J. DeStefano and J. L. Burmeister, *Inorg. Chem.*, 10, 998 (1971).

(8) J. Burmeister, *Coord. Chem. Rev.*, 1, 205 (1966).

(9) J. Burmeister, *Coord. Chem. Rev.*, 3, 225 (1968).

(10) C. Pecile, *Inorg. Chem.*, 5, 210 (1966).

(11) H.-H. Schmidtke, *J. Amer. Chem. Soc.*, 87, 2522 (1965).

However, D. Forster (*Inorg. Chem.*, 11, 1686 (1972)) has reported considerable solvent dependence in the relative affinities of some Ir(III) complexes for hard vs. soft halides.

(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 164.

(13) K. Nakamoto, J. Fujita, and H. Murata, *J. Amer. Chem. Soc.*, 80, 4817 (1958).

(14) F. Basolo and G. S. Hammaker, *J. Amer. Chem. Soc.*, 82, 1001 (1960).

(15) F. Basolo and G. S. Hammaker, *Inorg. Chem.*, 1, 1 (1962).

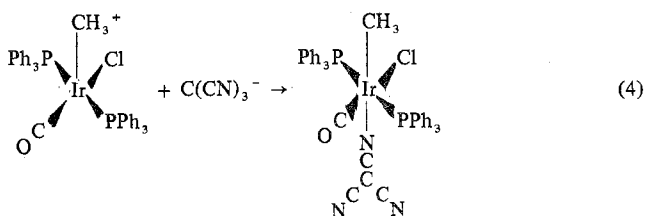
While the  $\text{NCO}^-$  ligand may bond through either O or N, the vast majority of complexes contain the N-bonded form. The first isolable linkage isomers of this anion were reported only very recently.<sup>16</sup> The N-bonded isomers in general show  $\nu_a(\text{NCO})$  from  $2170$  to  $2270\text{ cm}^{-1}$  and  $\nu_s(\text{NCO})$  in the region of  $1300$ – $1480\text{ cm}^{-1}$  with bends in the  $520$ – $670\text{ cm}^{-1}$  region.<sup>17</sup> Judging from infrared data the  $\text{NCO}^-$  complex reported here also is N bonded since a Nujol mull of the complex exhibits a broad  $\nu_a(\text{NCO})$  at  $2217\text{ cm}^{-1}$ ,  $\nu_s(\text{NCO})$  at  $1337\text{ cm}^{-1}$ , and one new band possibly assignable to  $\delta(\text{NCO})$  at  $597\text{ cm}^{-1}$ .

The nitrate compound  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{NO}_3)$  shows unique bands at  $1465$  and  $1275\text{ cm}^{-1}$  and a weak band at  $1015\text{ cm}^{-1}$ . There also is a band at  $1252\text{ cm}^{-1}$  but it is difficult to distinguish whether this is new or due to intensification of a band in this region which is seen in all of the spectra of these complexes. Unfortunately, the separation between the  $1465$ - and  $1275\text{ cm}^{-1}$  bands is not sufficient to allow unambiguous determination of the mode of bonding of the  $\text{NO}_3^-$  group in this complex.<sup>18,19</sup> Attempts to use Raman polarization data on the highest frequency band to distinguish between unidentate or bidentate bonding were unsuccessful because of the compound's low solubility.

Beck, *et al.*,<sup>20</sup> have carried out extensive synthetic and vibrational studies of azido complexes which are germane to the present work. Our azido complex shows the expected bands with  $\nu_a(\text{NNN})$  at  $2027\text{ cm}^{-1}$  in a Nujol mull and at  $2024\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  solution. The  $\nu_s(\text{NNN})$  which overlaps a parent band is seen at  $1255\text{ cm}^{-1}$  in a Nujol mull. The assignment of the  $\delta(\text{NNN})$  absorption is not as straightforward but there are two new weak to medium bands at  $650$  and  $585\text{ cm}^{-1}$  which may be due to this absorption. A band similar to the  $650\text{ cm}^{-1}$  band is also seen in the N-bonded  $\text{C}(\text{CN})_3^-$  complex while the  $585\text{ cm}^{-1}$  band is absent.

The acetato complex shows the expected three CO stretches at  $2044$ ,  $1588$ , and  $1330\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$ . The  $2044\text{ cm}^{-1}$  band arises from the coordinated carbon monoxide while the other two are characteristic of a complexed unidentate acetate group—the separation between the two acetate CO stretches being smaller for bidentate acetate groups.<sup>21</sup>

The  $\text{C}(\text{CN})_3^-$  group appears to be bonded to the metal through one of the "hard" cyanide nitrogen atoms.<sup>22</sup> Three CN stretches are observed in the mull spectrum with two strong absorptions due to the uncomplexed cyanides at  $2173$  and  $2168\text{ cm}^{-1}$  and a medium absorption due to the complexed CN at  $2223\text{ cm}^{-1}$  (eq 4). In addition, a new strong absorption was seen at  $1530\text{ cm}^{-1}$ .



The  $\text{Pt}(\text{CN})_4^{2-}$  ligand is unique in having a double negative

(16) S. J. Anderson, A. H. Norbury, and J. Songstad, *J. Chem. Soc., Chem. Commun.*, 37 (1974).

(17) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 191.

(18) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 172.

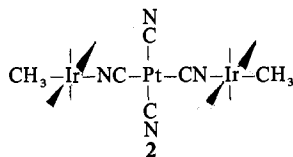
(19) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 4, 804 (1965).

(20) W. Beck, W. P. Fehlhammer, P. Pollmann, E. Schvieger, and K. Feldt, *Chem. Ber.*, 100, 2335 (1967).

(21) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1632 (1965).

(22) W. Beck, K. Schorpp, C. Oetker, R. Schlodder, and H. S. Smedal, *Chem. Ber.*, 106, 2144 (1973).

charge which results in the formation of a neutral complex incorporating two iridium moieties. Cyanide stretching frequencies are observed at 2170 and 2134  $\text{cm}^{-1}$  in  $\text{CHCl}_3$  solution. This is the pattern expected for trans bridging cyanides and terminal cyanides, as depicted in 2.



In the solid-state infrared spectrum of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$  two strong SO stretching frequencies are observed at 1347 and 1224  $\text{cm}^{-1}$ . These represent significant increases over typical asymmetric and symmetric frequencies of ionic fluorosulfates (1280  $\pm$  10 and 1075  $\pm$  10  $\text{cm}^{-1}$ ). Similar increases are observed (to 1323 and 1210  $\text{cm}^{-1}$ ) for the  $\text{SO}_3\text{CF}_3^-$  derivative, indicating for both compounds that the anion is bound to the metal, presumably through oxygen.

The SO stretching frequencies of the  $\text{S}_2\text{O}_2\text{C}_7\text{H}_7$  group are also found at higher frequencies in the metal complex than in the free ion. However, in this case we believe that bonding occurs through sulfur as found in alkyl thiosulfates and all structurally characterized monodentate thiosulfate complexes.<sup>23</sup> For both the latter two classes of compounds the SO stretching modes occur at higher frequencies than in the corresponding anion ( $\text{S}_2\text{O}_2\text{C}_7\text{H}_7^-$  or  $\text{S}_2\text{O}_3^{2-}$ ).

**Concluding Remarks.** Vaska has shown that the  $\nu_{\text{CO}}$  may be correlated with the electron-withdrawing ability of the trans X group in square-planar  $\text{Ir}(\text{X})(\text{CO})(\text{PPh}_3)_2$  compounds.<sup>24</sup> However, for the octahedral complexes discussed here (Table II), we have been unable to find a correlation between the  $\nu_{\text{CO}}$  and any simple properties of the X groups cis to the CO. This finding is in harmony with the general observations that the electronic interaction of trans ligands is generally much stronger than for those cis to each other.

The mutually trans arrangement of  $\text{CH}_3$  and  $\text{SO}_3\text{F}$  (or  $\text{SO}_3\text{CF}_3$ ) in  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$  must represent the thermodynamically favored form owing to the lability of the complex under the preparative conditions. This structure conforms to Pearson's idea of antisymbiosis in which a soft ligand ( $\text{CH}_3$  in this case) attached to a soft metal (Ir) promotes the coordination of a hard ligand in preference to a soft ligand in the trans position.<sup>25</sup> In somewhat different language, the very strong  $\sigma$  trans labilizing  $\text{CH}_3$  ligand weakens covalent bonds trans to it. Therefore, the most stable configuration involves the more covalent ligands cis to  $\text{CH}_3$  and the most ionic ligand,  $\text{SO}_3\text{F}$ , trans. These systematics also apply to the complexes with NCS or  $\text{NO}_2$  trans to  $\text{CH}_3$ , where coordination through the harder atom (N and O, respectively) was found.

Reactions analogous to (2) should provide a general synthetic route to a wide variety of metal-alkyl complexes. The key to this reaction is the high lability of metal-OSO<sub>2</sub>F and metal-OSO<sub>2</sub>CF<sub>3</sub> linkages. For general synthetic purposes the fluorosulfate and trifluoromethyl sulfate ions offer several advantages over the more commonly used weakly coordinating anions  $\text{ClO}_4^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ . Unlike the

former,  $\text{SO}_3\text{F}^-$  and  $\text{SO}_3\text{CF}_3^-$  are not strong and treacherous oxidizing agents, and unlike the latter two, they have little tendency to lose  $\text{F}^-$ .

## Experimental Section

Organic solvents were purified by distillation from appropriate dehydrating agents under an  $\text{N}_2$  atmosphere and were stored under  $\text{N}_2$  over appropriate desiccants. The carbo cation reagents,  $\text{CH}_3\text{SO}_3\text{F}$  and  $\text{CH}_3\text{SO}_3\text{CF}_3$  (Aldrich), were purified by trap-to-trap distillation under high vacuum and were stored under  $\text{N}_2$ . The parent  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  was prepared by published methods.<sup>26</sup> Infrared spectra were determined on Beckman IR-9 or IR-12 spectrometers which were calibrated against polystyrene or water vapor. Spectra of solid samples were taken from Nujol, Fluorolube, or hexachlorobutadiene mulls between KBr plates or polyethylene sheets. Mid-infrared solution studies were conducted in  $\text{CH}_3\text{NO}_2$  or  $\text{CH}_2\text{Cl}_2$  using liquid cells with 1-mm spacing between NaCl windows. Conductivity measurements were made with an Industrial Instruments Model RC 16B1 conductivity bridge. A Perkin-Elmer R20-B (60 MHz) instrument was used to record the  $^1\text{H}$  nuclear magnetic resonance spectra which were obtained from  $\text{CDCl}_3$  (Norell Chemical Co.) solutions. Chemical shifts relative to  $\text{CHCl}_3$  were determined from the frequency counter. A Mechrolab 302 osmometer was used for the molecular weight determinations. Elemental analyses were performed by H. Beck of this department. Decomposition points were obtained on samples sealed in capillary tubes under  $\text{N}_2$ .

**Chloro(methyl)fluorosulfatocarbonylbis(triphenylphosphine)iridium(III),  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$ .** To 6.18  $\times 10^{-1}$  mmol of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  in 60 ml of dry, air-free benzene was added 2 ml (25 mmol) of  $\text{CH}_3\text{SO}_3\text{F}$ . The solution was vigorously stirred until the color dissipated (1–2 hr) and was then concentrated to about half of the original volume by removal of the solvent under vacuum. Addition of an equal volume of dry, air-free heptane resulted in precipitation of the white solid,  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$ . Filtration of this product under  $\text{N}_2$  followed by washings with three 10-ml portions of pentane and drying under vacuum yielded the air-stable solid which could then be recrystallized from  $\text{CHCl}_3$ -heptane.

*Anal.* Calcd for  $\text{C}_{38}\text{H}_{33}\text{ClFO}_4\text{SP}_2\text{Ir}$ : C, 51.05; H, 3.69; Cl, 3.97; F, 2.12. Found: C, 51.24; H, 3.95; Cl, 4.03; F, 2.37.

**Chloro(methyl)trifluoromethylsulfatocarbonylbis(triphenylphosphine)iridium(III),  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{CF}_3)$ .** The preparation of this complex was analogous to that of the fluorosulfate analog. However, the product precipitated from solution more readily in this case.

*Anal.* Calcd for  $\text{C}_{39}\text{H}_{33}\text{ClF}_3\text{O}_4\text{SP}_2\text{Ir}$ : C, 49.61; H, 3.52. Found: C, 48.88; H, 3.36.

A typical preparation of the  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{X})$  complex, where X = F, Cl, Br, or I, follows. A 100-mg sample of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{CF}_3)$  was dissolved in 5 ml of  $\text{CH}_3\text{NO}_2$  in air to give a very pale yellow solution. A 20% excess of the tetraalkylammonium halide dissolved in  $\text{CH}_3\text{NO}_2$  was then added to the vigorously stirred parent solution. After 5–10 min the white or off-white precipitate was filtered from solution and washed with several portions of cold diethyl ether. The complex was then recrystallized from  $\text{CHCl}_3$ -heptane and dried under vacuum.

When X = NCS, NCO,  $\text{N}_3$ , ONO,  $\text{NO}_3$ ,  $\text{CH}_3\text{COO}$ ,  $\text{S}_2\text{O}_2\text{C}_7\text{H}_7$ , Pt(CN)<sub>4</sub>, or C(CN)<sub>3</sub>, the sodium or potassium salts of the appropriate anions were added as  $\text{H}_2\text{O}$  solutions instead of  $\text{CH}_3\text{NO}_2$  solutions. (To achieve the proper stoichiometry 1 mol of aqueous  $\text{K}_2\text{Pt}(\text{CN})_4$  was added per 2 mol of the iridium complex.)

**Acknowledgment.** This research was supported by the National Science Foundation through Grant GP-28878.

**Registry No.**  $\text{CH}_3\text{SO}_3\text{F}$ , 421-20-5;  $\text{CH}_3\text{SO}_3\text{CF}_3$ , 333-27-7;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , 15318-31-7;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{F})$ , 52154-79-7;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{SO}_3\text{CF}_3)$ , 52133-41-2;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{S}_2\text{O}_2\text{C}_7\text{H}_7)$ , 52133-42-3;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)\text{F}$ , 52133-43-4;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)\text{Cl}$ , 33394-14-8;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)\text{Br}$ , 52133-44-5;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{NO}_3)$ , 52133-45-6;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{CH}_3\text{COO})$ , 52154-80-0;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{NCS})$ , 52133-46-7;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{NCO})$ , 52133-47-8;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{N}_3)$ , 52133-48-9;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{ONO}_2)$ , 52133-49-0;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)(\text{C}(\text{CN})_3)$ , 52133-50-3;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)_2\text{Pt}(\text{CN})_4$ , 52133-40-1;  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{CH}_3)\text{I}$ , 24315-50-2.

(26) J. P. Colman, C. T. Sears, Jr., and M. Kubota, *Inorg. Syn.*, 11, 103 (1968).

(23) A. N. Freedman and B. P. Straughan, *Spectrochim. Acta*, Part A, 27, 1455 (1971).

(24) L. Vaska and J. Peone, Jr., *J. Chem. Soc. D*, 418 (1971).

(25) R. G. Pearson, *Inorg. Chem.*, 12, 712 (1973); also J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 2745 (1968).