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TRIFLUOROMETHYL AND MIXED HYDRIDO TRIFLUOROMETHYL COMPLEXES OF IRIDIUM(III) AS POTENTIAL PRECURSORS OF AN IRIDIUM(I) TRIFLUOROMETHYL COMPLEX

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Summary

Abstraction of iodide from $Ir(CF_3)ClI(CO)(PPh_3)_2$ (**1**) by $AgSbF_6$ in the presence of acetonitrile yields the cationic complex $[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+ [SbF_6]^-$ (**2**). The acetonitrile group of **2** is readily displaced, and **2** reacts with *para*-tolyl isocyanide to yield $[Ir(CF_3)Cl(CN\text{-}p\text{-tolyl})(CO)(PPh_3)_2]^+ [SbF_6]^-$ (**3**). The addition of NaOMe to **3** results in the methoxyester complex $Ir(CF_3)(COOMe)Cl(CN\text{-}p\text{-tolyl})(PPh_3)_2$ (**4**). The acetonitrile ligand of **2** is also displaced by anions, including H^-. Thus, **2** reacts with $LiEt_3BH$ to give $Ir(CF_3)HCl(CO)(PPh_3)_2$ (**5**), in which the hydrido and trifluoromethyl ligands are mutually *trans*. In contrast, the addition of excess $NaBH_4$ to **2** affords the novel dihydrido complex *trans*-$Ir(CF_3)H_2(CO)(PPh_3)_2$ (**6**). Investigations into the potential use of **5** and **6** as precursors of an iridium(I) complex such as $Ir(CF_3)(CO)(PPh_3)_2$ are also described.

Introduction

A number of recent investigations [1–6] have been concerned with the susceptibility of the CF_3 ligand in d^6 complexes towards electrophilic attack. In order to extend these reactivity studies, we have attempted to prepare a d^8 trifluoromethyl complex of iridium by the reduction of a suitable d^6 compound. The target species, $Ir(CF_3)(CO)(PPh_3)_2$ (or a coordinatively saturated equivalent), would be the trifluoromethyl analogue of Vaska's compound. The similarity in size and electronegativity of the CF_3 group to the halogens suggests that the preparation of such a compound is a viable prospect. Since a frequently successful [7] strategy for the d^6 to d^8 reduction involves the deprotonation of d^6 hydrido complexes, we initially aimed for a route to a hydrido trifluoromethyl compound from the available [8] iridium(III) complex $Ir(CF_3)ClI(CO)(PPh_3)_2$.

The stability of the few known examples of mixed hydrido trifluoromethyl compounds [9,10] towards reductive elimination of CHF_3 contrasts with the tend-

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ency of similar hydrido methyl complexes [11] towards methane elimination, reflecting the greater strength of the metal–carbon bond in transition metal perfluoroalkyl complexes relative to the corresponding alkyl species. In this paper we describe the synthesis of two thermally stable hydrido trifluoromethyl complexes of iridium(III). The reduction through deprotonation of these compounds to the desired iridium(I) trifluoromethyl compound has not yet been achieved.

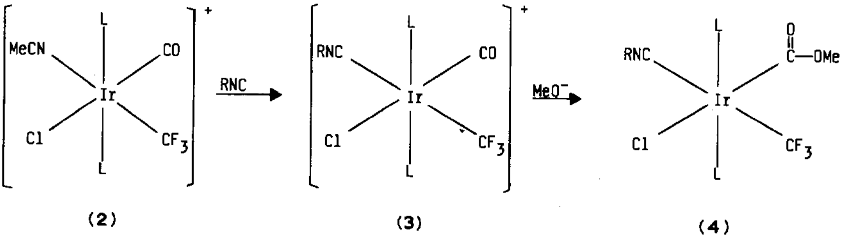
Results and discussion

That the *trans*-influence of the CF_3 group is sufficient to allow abstraction of a *trans*-halide by silver salts has been demonstrated for platinum(II) [9,12] and ruthenium(II) [10] trifluoromethyl compounds. Similarly, $Ir(CF_3)ClI(CO)(PPh_3)_2$ (**1**), prepared by a modification of the method of Blake et al. [8], reacts with $AgSbF_6$ in the presence of acetonitrile to yield $[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+ [SbF_6]^-$ (**2**) and a precipitate of AgI. This suggests that the iodine atom is *trans* to the CF_3 group in **1**. The presence of a band attributable to $\nu(IrCl)$ at the relatively high value of 322 cm^{-1} in the IR spectrum of **1** supports this proposed geometry. By comparison, the IR spectrum of $Ir(CF_3)Cl_2(CO)(PPh_3)_2$ (**7**) shows $\nu(IrCl)$ absorbtions at 329 and 296 cm^{-1}.

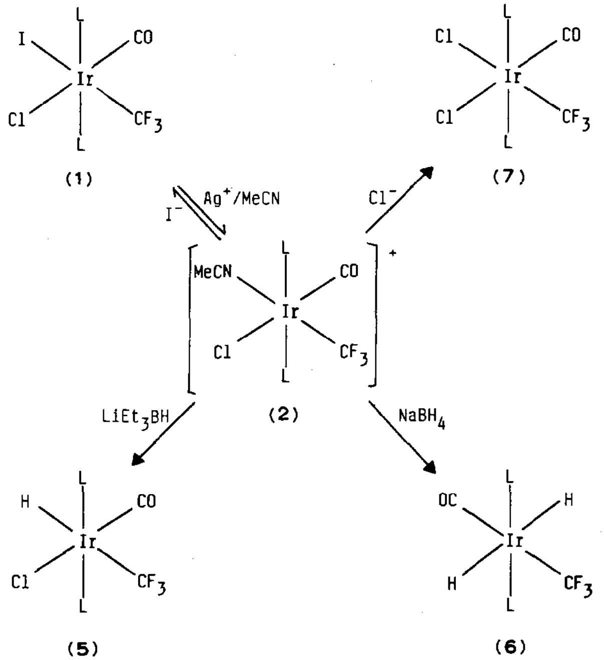
The acetonitrile ligand of **2** is labile, as illustrated by the rapid reaction of **2** with *para*-tolyl-isocyanide to give a new cationic complex, $[Ir(CF_3)Cl(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2]^+ [SbF_6]^-$ (**3**), as depicted in Scheme 1. The action of sodium methoxide on **3** results in a neutral methoxyester compound, $Ir(CF_3)(COOMe)Cl(CN\text{-}p\text{-}tolyl)(PPh_3)_2$ (**4**).

Furthermore, the acetonitrile ligand of **2** is readily displaced by anionic groups, as shown in Scheme 2. Thus, the reaction of **2** with I^- returns the starting material, **1**, while the addition of Cl^- to **2** provides an alternative [8] route to $Ir(CF_3)Cl_2(CO)(PPh_3)_2$ (**7**).

The preparation of the monohydrido compound $Ir(CF_3)HCl(CO)(PPh_3)_2$ (**5**) was achieved by the action of one equivalent of $LiEt_3BH$ on the cationic complex **2**. The presence of a hydride ligand was demonstrated by the IR (see Table 1) and ^1H NMR (see Table 2) spectra. In the IR spectrum of **5**, the $\nu(IrH)$ absorbtion occurs at 2031 cm^{-1}, a rather low value consistent with the *trans*-influence of the trifluoromethyl group. The ^1H NMR spectrum of **5** consists of a quartet of triplets centred at δ −9.06 ppm, resulting from coupling of the proton with both fluorine and phosphorus nuclei.



SCHEME 1. L = PPh_3, R = *p*-tolyl.



SCHEME 2. L = PPh_3.

TABLE 1

IR[a] DATA (cm^{-1}) FOR TRIFLUOROMETHYLIRIDIUM COMPLEXES

Compound[b]	ν(CO)	ν(CF)	Other bands[b]
$[Ir(CF_3)Cl(MeCN)(CO)L_2]^+[SbF_6]^-$ (2)	2118	1114, 1098, 1054, 1037, 1028, 1001m	336m ν(IrCl) 2314vs (MeCN) 661vs, 294vs (SbF_6)
$[Ir(CF_3)Cl(CNR)(CO)L_2]^+[SbF_6]^-$ (3)	2113	1106, 1097, 1073m, 1049, 1031, 998m	328w ν(IrCl) 2235m ν(NC); 1501m, 821m (RNC) 660vs, 292vs (SbF_6)
$Ir(CF_3)(COOMe)Cl(CNR)L_2$ (4)	–	1092, 1033, 1011, 1003, 997, 991, 981m, 973m	329w ν(IrCl) 2185 ν(NC); 1503m, 819m 3332vw, 1673 νCO) 938m
$Ir(CF_3)HCl(CO)L_2$ (5)	2076	1082, 1006, 995, 998, 976	322m ν(IrCl) 2031m ν(IrH) 857w δ(IrH)
$Ir(CF_3)H_2(CO)L_2$ (6)	2069, 2041[c] 2049[d]	1091, 1076m, 1008, 1001, 984, 973	1781 ν(IrH) 831m, 815mδ(IrH)

[a] Measured as Nujol mulls. All bands strong unless otherwise indicated. [b] L = PPh_3, R = *p*-tolyl. [c] Solid state splitting. [d] Spectrum obtained in CH_2Cl_2 solution.

TABLE 2

^{1}H NMR DATA[a] (δ (ppm), J (Hz)), FOR TRIFLUOROMETHYLIRIDIUM COMPLEXES

Compound[b]	Chemical shift (δ)
$[Ir(CF_3)Cl(MeCN)(CO)L_2]^+[SbF_6]^-$ (2)	1.55, s, 3H, CH_3CN 7.2–8.1, m, 30H, $P(C_6H_5)_3$
$[Ir(CF_3)Cl(RNC)(CO)L_2]^+[SbF_6]^-$ (3)	2.33, s, 3H, $CH_3C_6H_4NC$ 6.72, m, 4H, $CH_3C_6H_4NC$ 7.0–8.2, m, 30H, $P(C_6H_5)_3$
$Ir(CF_3)(COOMe)Cl(RNC)L_2$ (4)	2.28, s, 3H, $CH_3C_6H_4NC$ 2.37, s, 3H, $COOCH_3$ 6.65, m, 4H, $CH_3C_6H_4NC$ 6.9–8.2, m, 30H, $P(C_6H_5)_3$
$Ir(CF_3)HCl(CO)L_2$[c] (5)	−9.06, qt, 1H, Ir–H, ^3J(HF), 24.2, ^2J(HP) 15.3 7.2–8.0, m, 30H, $P(C_6H_5)_3$
$Ir(CF_3)H_2(CO)L_2$[c] (6)	−7.62, tq, 2H, $Ir(H)_2$, ^2J(HP) 15.0, ^3J(HF) 9.5 7.1–8.2, m, 30H, $P(C_6H_5)_3$

[a] In $CDCl_3$ solution unless otherwise indicated. [b] L = PPh_3, R = *p*-tolyl. [c] In CD_2Cl_2 solution.

In contrast, the reaction of **2** with excess $NaBH_4$ in ethanol suspension yields the novel *trans*-dihydrido complex $Ir(CF_3)H_2(CO)(PPh_3)_2$ (**6**). The monohydrido species **5** is in fact also formed in up to 40% yield, although the proportion of **5** can be minimized by carrying out the reaction on a small scale with finely ground starting material. It seems likely that **5** is the initial product but will react no further once it has crystallised. However, the mechanism of the process by which **6** is formed remains unclear.

The proposed *trans* geometry of **6** is indicated by the presence of one strong ν(IrH) absorbtion in the IR spectrum at 1781 cm^{-1}. The extremely low position of this band, typical of *trans*-dihydrido compounds, is consistent with the high *trans*-influence of the hydride ligand. A *trans* geometry is further suggested by the ^{1}H NMR spectrum, which reveals only one set of hydride resonances at δ −7.62 ppm integrating for two hydrogen nuclei. In this case, the signal appears as a triplet of quartets due to a marked decrease in the value of the H–F coupling constant, ^3J(HF), compared to the corresponding value for **5**. Such a decrease is in accord with the common observation of a stronger coupling between nuclei which are mutually *trans* about a metal centre relative to nuclei which have a *cis* arrangement.

Both **5** and **6** failed to respond to various deprotonation attempts, nor was the chloride ligand of **5** sufficiently labile for the synthesis of an appropriate cationic, and thus more acidic, hydrido trifluoromethyl compound.

Experimental

Benzene and THF were dried and deoxygenated by distillation over sodium/benzophenone/triglyme under an atmosphere of nitrogen. Characterisation of new compounds was achieved by means of elemental analysis, IR and ^{1}H NMR spectroscopy. Analytical data were obtained from the Microanalytical Laboratory, University of Otago. IR spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 597 spectrometer or a Pye Unicam SP3-300 spectrometer as Nujol mulls or dichloromethane solutions between KBr plates. ^1H NMR spectra were recorded on a Varian Associates T60 or E.M. 360L spectrometer, or on a JEOL FX-60 fourier-transform spectrometer using tetramethylsilane as an internal calibrant. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. Iridium trichloride was obtained commercially from Johnson–Matthey Chemicals Ltd. $IrCl(CO)(PPh_3)_2$ [13] and CF_3I [14] were prepared by the literature methods.

$Ir(CF_3)ClI(CO)(PPh_3)_2$

(i) $IrCl(CO)(PPh_3)_2$ (3.0 g, 3.8 mmol) was partially dissolved in deoxygenated benzene (150 ml) in a Fischer–Porter bottle under nitrogen and cooled to −78°C. CF_3I (13 ml, 160 mmol) was added, and the bottle was fitted to a closed pressure gauge and allowed to warm to room temperature. After stirring for 6 d at a pressure of ca. 10 psi, the resultant orange solid was purified by the addition of excess $NaBH_4$ to a stirred dichloromethane/ethanol solution, yielding cream crystals upon reduction of the solvent volume. The product was further purified by chromatography on a 40 × 3 cm column of silica gel using a 3/2 ratio of dichloromethane/n-hexane as the eluant. Recrystallisation from dichloromethane/ethanol afforded pale cream crystals (2.75 g, 73%). M.p. 246–248°C. Anal. Found: C, 46.91; H, 3.52; F, 5.41. $C_{38}H_{30}ClF_3IIrOP_2$ calcd.: C, 46.76; H, 3.10; F, 5.84%.

(ii) $[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+ [SbF_6]^-$ (100 mg, 0.09 mmol) was dissolved in dichloromethane (5 ml) and a solution of NaI (18 mg, 0.12 mmol) in ethanol (50 ml) was added. The solution was stirred for 10 min, during which time a fine cream solid crystallised. This was collected after removal of dichloromethane and washed with ethanol then n-hexane (80 mg, 92%).

$[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+ [SbF_6]^-$

$Ir(CF_3)ClI(CO)(PPh_3)_2$ (2.75 g, 2.8 mmol) was dissolved in dichloromethane (700 ml) and $AgSbF_6$ (1.27 g, 3.7 mmol) in acetonitrile (150 ml) was added to the vigorously stirred mixture. After 2 h the resultant suspension was filtered through a celite pad. Removal of solvent at reduced pressure gave the white product and recrystallisation from dichloromethane/ethanol yielded white needles (2.41 g, 76%). M.p. 206–210°C. Anal. Found: C, 42.64; H, 3.36; N, 1.23; F, 14.25. $C_{40}H_{33}ClF_9IrNOP_2Sb$ calcd.: C, 42.67; H, 2.95; N, 1.24; F, 15.18%.

$Ir(CF_3)Cl_2(CO)(PPh_3)_2$

$[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+ [SbF_6]^-$ (100 mg, 0.09 mmol) was dissolved in dichloromethane (5 ml) and a solution of NaCl (7 mg, 0.12 mmol) in ethanol (50 ml) was added. After 10 min, pearly white crystals had formed. These were collected after removal of dichloromethane and washed with ethanol and n-hexane (70 mg, 89%). M.p. 220–222°C. Anal. Found: C, 51.63; H, 3.78; F, 6.14. $C_{38}H_{30}Cl_2F_3IrOP_2$ calcd.: C, 51.59; H, 3.42; F, 6.44%.

$Ir(CF_3)HCl(CO)(PPh_3)_2$

$[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+ [SbF_6]^-$ (100 mg, 0.09 mmol) was stirred in THF under nitrogen and a THF solution of $LiEt_3BH$ (0.13 ml of 1 mol l^{-1}; 0.13 mmol) was added. Addition of n-hexane and removal of solvent under reduced pressure yielded a grey solid which was dissolved in dichloromethane and filtered through a celite pad. Crystallisation from dichloromethane/ethanol yielded white crystals (75 mg, 99%). M.p. 207–208°C. Anal. Found: C, 53.43; H, 3.96; F, 6.31. $C_{38}H_{31}ClF_3IrOP_2$ calcd.: C, 53.68; H, 3.68; F, 6.70%.

$Ir(CF_3)H_2(CO)(PPh_3)_2$

$[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+$ $[SbF_6]^-$ (< 90 mg, 0.08 mmol) was finely ground and suspended in vigorously stirred ethanol (10 ml), and a filtered solution of $NaBH_4$ (20 mg, 0.53 mmol) in ethanol (40 ml) was added. After 30 min the solvent was removed under reduced pressure, and the product redissolved in dichloromethane and filtered through a celite pad. Crystallisation followed by recrystallisation from dichloromethane/ethanol afforded white crystals of the title compound (55 mg, 84%). M.p. 172–173°C. Anal. Found: C, 55.54; H, 4.45; F, 6.46. $C_{38}H_{32}F_3IrOP_2$ calcd.: C, 55.95; H, 3.95; F, 6.99%.

$[Ir(CF_3)Cl(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2]^+$ $[SbF_6]^-$

$[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]^+$ $[SbF_6]^-$ (700 mg, 0.62 mmol) was dissolved in dichloromethane (40 ml) and a solution of *para*-tolyl-isocyanide (80 mg, 0.68 mmol) in ethanol (10 ml) was added with stirring. Addition of ethanol and removal of solvent under reduced pressure gave the white crystalline product. Recrystallisation from dichloromethane/ethanol yielded large white crystals (750 mg, > 99%). M.p. 258–260°C. Anal. Found: C, 46.06; H, 3.43; N, 1.27; F, 14.29. $C_{46}H_{37}ClF_9IrNOP_2Sb$ calcd.: C, 45.96; H, 3.10; N, 1.17; F, 14.22%.

$Ir(CF_3)(COOMe)Cl(CN\text{-}p\text{-}tolyl)(PPh_3)_2$

$[Ir(CF_3)Cl(CN\text{-}p\text{-}tolyl)(CO)(PPh_3)_2]^+$ $[SbF_6]^-$ (500 mg, 0.21 mmol) was dissolved in dichloromethane (30 ml) and a solution of NaOMe prepared by dissolving sodium (250 mg, 10.9 mmol) in methanol (20 ml) was added. The solution was stirred for 5 min followed by complete removal of solvent under reduced pressure. The product was dissolved in dichloromethane and the resulting solution was twice washed with water and dried over $MgSO_4$. Addition of ethanol and removal of solvent under reduced pressure yielded a cream solid which was recrystallised from dichloromethane/ethanol to give pale cream crystals (270 mg, 65%). M.p. 187–190°C. Anal. Found: C, 56.37; H, 4.42; N, 1.55; F, 5.63. $C_{47}H_{40}ClF_3IrNOP_2$ calcd.: C, 56.60; H, 4.04; N, 1.40; F, 5.71%.

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