Journal of Organometallic Chemistry, *445* (1993) 283–286

JOM 23147

The synthesis of ionic iridium(III) carbene complexes of the type $[Ir\{=CR{-}NHMe\}Cl(OSO_2CF_3)(CO)(PPh_3)_2]^+[O_3SCF_3]^-$

B.L. Booth and A.C. Wickens

Department of Chemistry, University of Manchester, Institute of Science and Technology, Manchester M60 1QD (UK)

(Received August 11, 1992)

Abstract

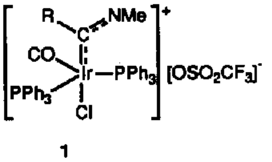
The title compounds in which R = C_6H_5, 4-MeC_6H_4, 4-EtC_6H_4 and CH_3 have been prepared in moderate to good yield by the reaction between $[IrHCl(O_3SCF_3)(CO)(PPh_3)_2]$ and the corresponding *N*-methylnitrilium triflate salts $[RC{\equiv}NMe]^+[O_3SCF_3]^-$.

1. Introduction

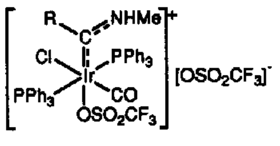
Since the first discovery of stabilized transition metal carbene complexes by Fischer and Maasböl [1] there has been considerable interest in this area, which has been the subject of several reviews [2–4]. Despite this interest, complexes containing the carbene moiety $[M(=CRNHR^1)]$ (R = alkyl or aryl, R^1 = alkyl or aryl) are relatively uncommon. Group 6 transition metal carbene complexes of this type have been prepared by reaction of other carbene [5] or carbyne complexes [6] with primary amines, and rhodium(III) complexes of this type have been prepared by the reaction of imidoyl chlorides with Rh^I complexes in the presence of HCl gas [7]. To our knowledge there has been no previous report of iridium(III) carbene complexes having this structure apart from a preliminary communication from our group [8].

In that earlier communication it was reported that reactions between Vaska's compound *trans*-$[IrCl(CO)(PPh_3)_2]$ and *N*-methylnitrilium (trifluoromethanesulfonate) (triflate) salts in dry chloroform gave mainly amorphous yellow solids, which were tentatively assigned the structure **1** on the basis of elemental analysis, IR and NMR spectroscopy, although it could not be established conclusively that they were simple monomers. In each case, formation of the yellow product was accompanied by low and variable yields of a corresponding white crystalline solid having the structure **2**. It was not clear at the time how this product was formed and why the yields were so variable, although it was suspected that the white solids might be connected with the presence of low concentrations of triflic acid arising from partial hydrolysis of the methyl triflate used in the preparation of the nitrilium salts.

A more detailed investigation of this reaction has now been undertaken and we report here that these same compounds can be prepared in moderate to good yields by the reaction of $[IrHCl(O_3SCF_3)(CO)(PPh_3)_2]$ with nitrilium triflate salts.



1



2 (a) R = C_6H_5
(b) R = *p*-$CH_3C_6H_4$
(c) R = *p*-$C_2H_5C_6H_4$
(d) R = CH_3

2. Results and discussion

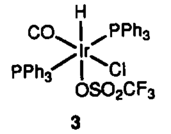
A bright yellow solution of Vaska's compound in dry chloroform rapidly turned fawn upon addition of *N*-methylbenzonitrilium triflate and 1 equivalent of triflic acid, and after 24 h the addition of diethyl ether gave a 64% yield of impure compound **2a** as a fawn precipitate. Attempts to extend this reaction to *N*-methylisobutyronitrilium salt resulted in a similar rapid colour change, but in this case a white solid separated after

---

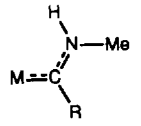
Correspondence to: Dr. B.L. Booth.

0022-328X/93/$6.00

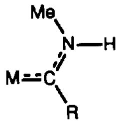
only 0.5 h. This solid was identified as the known compound $[IrHCl(O_3SCF_3)(CO)(PPh_3)_2]$ (**3**), which has been prepared previously by the oxidative addition of triflic acid to Vaska's compound [9,10]. The reaction between Vaska's compound and triflic acid is very rapid at room temperature, and this result implied that the hydride **3** might be involved in the synthesis of the complexes of type **2**. Consequently, a solution of **3** in chloroform added dropwise to a solution of *N*-methylbenzonitrilium triflate in the same solvent was found to give **2a** in 66% yield upon precipitation with diethyl ether after 24 h at room temperature. A similar procedure was used for the preparation of the compounds **2b–d** in the yields shown.



3



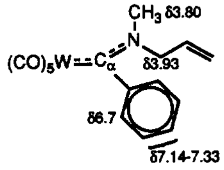
4a



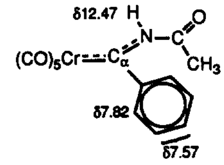
4b

In their IR spectra the compounds **2a–d** showed two N–H stretching vibrations at *ca.* 3200 and 3180 cm^{-1}, suggesting that they might be mixtures of *syn*- (**4a**) and *anti*- (**4b**) isomers; similar isomers have been identified for the chromium carbene complex [Cr{=CMeNHMe}$(CO)_5$] [11]. This was confirmed by the ^1H NMR spectra (*vide infra*). The IR spectra also show a strong sharp terminal metal carbonyl stretching vibration at *ca.* 2095 cm^{-1} and a strong sharp band at *ca.* 1600 cm^{-1} for a C=N stretching frequency. These bands are consistent with those reported by Lappert and Oliver [7] for the complexes $[Rh[{=}CPhNHR]Cl_3(CO)(PPh_3)]$ (R = Me, Et, ^iPr). The compounds **2a–d** all show strong bands in the IR spectra at *ca.* 1340, 1280, 1265, 1235, 1155, 1030 and 630 cm^{-1} due to the triflate groups. The band at 1340 cm^{-1} is characteristic of a monodentate triflate ligand [12] and the number and complexity of these bands is indicative of the presence of both a covalently bound monodentate and an ionic triflate group. Support for this comes from the ^{19}F NMR spectra, which show two signals at δ 0.5 ($\pm$0.1) and δ 2.5 ($\pm$0.1) ppm to low field of TFA reference.

The ^1H NMR spectra of complexes **2a–c** showed two bands at δ 2.55 and 2.58 ppm in the intensity ratio of 4-8:1, both with a 5 Hz coupling to NH, for the *syn*- and *anti-N*-methyl protons. On the basis of the data available, it is not possible to decide which isomer is the major one, but, intuitively, it would be expected that the *anti* or *E* isomer might predominate. These chemical shift values and the observed coupling constant is entirely consistent with those found for the rhodium complex $[Rh\{{=}CPhNHMe\}Cl_3(CO)(PPh_3)]$ [7]. The NH signals at δ 10.2 $\pm$ 0.1 ppm in complexes **2a–c** and at δ 9.25 ppm in **2d** were broad and no coupling could be distinguished. In the spectrum of compound **2d** the NMe appeared as a single 5 Hz doublet at δ 2.43 and there was no evidence for geometrical isomers in this compound. The C-methyl protons appeared at δ 2.73, which is in the range reported previously for the similar chromium and tungsten complexes $[M\{{=}CMeNHMe\}(CO)_4L]$ [M = Cr, L = PPh_3 (δ 2.4 ppm); M = W, L = CO (δ 2.92 ppm)] [11]. The ^1H NMR spectra of the aromatic derivatives **2a–c** are interesting as the protons *ortho* to the carbene C atom are considerably shielded and appear in the chemical shift range of δ 5.93–6.00 ppm, implying that the carbene ligand has a more powerful shielding effect than an amino or alkoxy group. A similar shielding effect has been reported for the tungsten(0) carbene complex **5** [13], but is unexpected for an iridium(III) complex and suggests that overlap of the nitrogen lone pair with the C_α atom of the carbene ligand is considerable. In this respect it is interesting that in the chromium(0) complex **6**, in which the nitrogen lone pair can be delocalized over the acyl carbonyl group, the carbene ligand appears to be deshielding and the hydrogens *ortho* to C_α have a chemical shift of δ 7.82 ppm [14]. In all cases the aryl complexes **2a–c** show an additional low intensity, 8 Hz doublet around δ 5.8 ppm for the *ortho* hydrogens of the minor geometrical isomer. ^{13}C NMR spectra could not be obtained on these compounds as they are not sufficiently soluble in $CDCl_3$ and decompose rapidly to Vaska's compound in deuterated polar solvents.



5

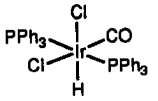


6

The ^{31}P NMR spectra of compounds **2a–c** show only one sharp signal at δ -7.6 ± 0.4 ppm, implying that the phosphine ligands have a *trans* arrangement. All the complexes are sensitive to hydroxylic solvents and addition of water or methanol to these compounds either in the solid state or in chloroform solution caused immediate and quantitative conversion into Vaska's compound, and for this reason we suggest the stereochemistry shown in **2a–c**. The sensitivity of the triflate ligand to dissociation in polar solvents and the ease of hydrolysis have frustrated all attempts to obtain crystals suitable for single crystal X-ray analysis.

Reactions between **3** and aliphatic *N*-methylnitrilium triflate salts (R = Et or ^nPr) under similar conditions appear to proceed in a similar manner, but the products are oils and the compounds appear to be much more susceptible to decomposition and so could not be isolated pure.

The mechanism of the formation of **2a–c** from compound **3** has not been investigated in any detail, but it seems probable that an essential first step in the reaction is dissociation of the weakly coordinated triflate ligand from **3** followed by coordination of the nitrilium salt to the iridium. Attempts to carry out a similar reaction between the iridium hydride **7** and *N*-methylbenzonitrilium triflate in dry chloroform resulted only in unchanged starting materials after more than 1 week at room temperature. Compound **7** is much less soluble in chloroform than **3**, but there was sufficient hydride in solution to expect evidence of some reaction if it had occurred.



7

3. Experimental details

All solvents and reactants were purified and dried by standard procedures. Reactions were carried out in flame-dried apparatus under oxygen- and moisture-free argon. Methyl triflate was either obtained commercially or was freshly prepared when required [12]. *N*-Methylnitrilium triflate salts [15], $[IrHCl_2(CO)(PPh_3)_2]$ [16] and $[IrCl(CO)(PPh_3)_2]$ [17] were prepared by standard procedures.

Infrared spectra were recorded on a Perkin–Elmer spectrophotometer PE 298 in the range 4000–600 cm^{-1}, and ^1H NMR spectra were recorded on a Bruker XL300 spectrometer, field frequency 300 MHz with tetramethylsilane as external reference. ^{19}F NMR spectra were recorded on a Perkin–Elmer R32 spectrometer at 86.4 MHz with trifluoroacetic acid as external reference, and ^{31}P NMR were recorded on a WP80 spectrometer at 32.44 MHz with phosphoric acid as external reference. Mass spectra were obtained by the fast atom bombardment technique in a 3-nitrobenzyl alcohol matrix.

3.1. Preparation of carbonylchlorohydrido(trifluoromethanesulphonato)bis(triphenylphosphine)iridium(III)

A solution of $[IrCl(CO)(PPh_3)_2]$ (0.50 g, 0.64 mmol) in chloroform (10 cm^3) was added to triflic acid (0.10 g, 0.64 mmol, 0.06 cm^3) in chloroform (5 cm^3). The volume was reduced to 10 cm^3, and diethyl ether was added until the mixture remained turbid. It was kept in a freezer for 2–3 h and the white solid that separated was washed with diethyl ether and the residual solvent was removed under high vacuum to yield white microcrystals of **3** (0.51 g, 85%), m.p. 229°C. Anal. Found: C, 49.3; H, 3.2; P, 6.6. $C_{38}H_{31}ClF_3O_4P_2S$ calc., C, 49.1; H, 3.4; P, 6.7%. ν_{max}(CO): 2060vs. ($CHCl_3$): δ_H ($CDCl_3$) −21.75 (1H, t, *J*(P–H) = 12Hz, Ir–H); 7.5 (30H, m, $2[PPh_3]$); δ_F ($CDCl_3$) 1.85 (s); δ_P +5.29 (s) ppm.

3.2. Preparation of $[Ir(C\{Ph\}{=}NHMe)Cl(OSO_2CF_3)(CO)(PPh_3)_2]^+[OSO_2CF_3]^-$

3.2.1. From **3**

A solution of **3** (0.27 g, 0.29 mmol) in chloroform (10 cm^3) was added by syringe to *N*-methylbenzonitrilium triflate (0.08 g, 0.30 mmol). The solution was protected from light and stirred for 24 h. Diethyl ether was added until the solution remained turbid. The solution was kept in the freezer for several hours and the solid obtained was washed with dry diethyl ether (3 × 5 cm^3) and dried under high vacuum to give a white air-stable solid, which was identified as compound **2a** (0.23 g, 66%), m.p. 189°C (with decomposition) (lit. [8] m.p. 184–186°C). Anal. Found: C, 46.7; H, 3.2; N, 1.3. $C_{47}H_{39}ClF_6IrNO_4P_2S_2$ calc., C, 47.1; H, 3.3; N, 1.2%. ν_{max} ($CHCl_3$): 3210w, 3160m, 3080m, 2930w, 2870w, 2095s, 1608s, 1485m, 1435w, 1395w, 1345s, 1280s, 1265s, 1235s, 1155s, 1095s, 1030s, 990s, 840vw, 710m, 630s cm^{-1}. δ_H ($CDCl_3$) 2.57 (3H, d, *J* = 5Hz, $NHCH_3$); 5.92 (2H, d, *J* = 8Hz, *ortho*); 7.43 (33H, m, $2[PPh_3]$, *meta* + *para*); 10.31 (1H, s, $NHCH_3$); δ_F 0.56 (s), 2.53 (s); δ_P ($CDCl_3$) −7.77 ppm. *m/z* 1048 (M − OSO_2CF_3); 899 (M − $2OSO_2CF_3$); 871 (M − $2OSO_2CF_3$ − CO); 636 (M − $2OSO_2CF_3$ − PPh_3 − H); 608 (M − $2OSO_2CF_3$ − CO − PPh_3 − H); 572 (M − $2OSO_2CF_3$ − CO − PPh_3 − H − Cl); 118 (100) (C{Ph}NMe).

3.2.2. From Vaska's compound

Triflic acid (0.10 g, 0.64 mmol, 0.06 cm^3) was added to a solution of *N*-methylbenzonitrilium triflate (0.17 g, 0.64 mmol) in chloroform (5 cm^3) at room temperature. Vaska's compound (0.50 g, 0.64 mmol) in chloroform (15 cm^3) was added and the mixture was protected from light and stirred for 24 h. Diethyl ether was added until the mixture remained turbid and the solution was kept at −10°C for 2 h. The precipitate obtained was washed with diethyl ether to give **2a** (0.49 g, 64%).

3.3. Preparation of $[Ir(C\{p\text{-}CH_3C_6H_4\}{=}NHMe)Cl(OSO_2CF_3)(CO)(PPh_3)_2]^+[OSO_2CF_3]^-$

Reaction between *N*-methyl-*p*-methylbenzonitrilium triflate (0.15 g, 0.53 mmol) and **3** (0.50 g, 0.53 mmol) under the conditions described above gave, after work-up, **2b** as a white solid (0.39 g, 60%), m.p. 176°C. Anal. Found: C, 47.3; H, 3.1; N, 1.1; S, 5.2. $C_{48}H_{41}ClF_6Ir$-

$NO_7P_2S_2$ calc., C, 47.6; H, 3.4; N, 1.2; S, 5.3%. $\nu_{max}(CHCl_3)$ 3200m, 3180w, 3060m, 2095s, 1595s, 1575sh, 1485s, 1435s, 1390w, 1340vs, 1280s, 1260s, 1240m, 1195s, 1175s, 1150s, 1090m, 1030m, 985s, 900m, 860w, 705m, 690s, 630s cm^{-1}. δ_H ($CDCl_3$) 2.43 (3H, s, *p*-CH_3); 2.55 (3H, d, $J = 5Hz$, $NHCH_3$); 5.93 (2H, d, $J = 8Hz$, *ortho*); 7.04 (2H, d, $J = 8Hz$, *meta*); 7.44 (30H, m, 2[PPh_3]); 10.18 (1H, br, s, N*H*CH_3); δ_F ($CDCl_3$) 0.5 (s), 2.4 (s); δ_P($CDCl_3$) −7.92 ppm. *m/z* 1063 ($M - OSO_2CF_3 + H$); 1062 ($M - OSO_2CF_3$); 913 ($M - 2OSO_2CF_3$); 885 ($M - 2OSO_2CF_3 - CO$); 650 ($M - 2OSO_2CF_3 - PPh_3 - H$); 623 ($M - 2OSO_2CF_3 - CO - PPh_3$); 586 ($M - 2OSO_2CF_3 - CO - PPh_3 - Cl - H$); 132 (100%) (C{*p*-$CH_3C_6H_4$}NMe).

3.4. *Preparation of [Ir(C{p-$CH_3CH_2C_6H_4$}=NHMe) Cl(OSO_24-CF_3)(CO)(PPh_3)$_2$]$^+$[OsO_2CF_3]$^-$*

Reaction between *N*-methyl-*p*-ethylbenzonitrilium triflate (0.08 g, 0.27 mmol) and **3** (0.25 g, 0.27 mmol) under the standard gave, after work up **2c** as a white solid (0.18 g, 55%), m.p. 179–181°C (with decomposition). Anal. Found: C, 47.7; H, 3.4; N, 1.1; P, 4.9. $C_{49}H_{43}ClF_6IrNO_7P_2S_2$ calc., C, 48.0; H, 3.5; N, 1.1; P, 5.1%. $\nu_{max}(CHCl_3)$ 3205m, 3180w, 3060m, 2970w, 2095s, 1600s, 1485m, 1435s, 1385w, 1345s, 1330sh, 1280s, 1255s, 1230s, 1200s, 1180m, 1155m, 1090m, 1030s, 985s, 845w, 705m, 690s, 630s cm^{-1}. δ_H ($CHCl_3$) 1.20 (3H, t, J=8Hz, CH_3); 2. 55 (3H, d, J=5Hz, $NHCH_3$); 2.72 (2H, q, J=8Hz, CH_2); 5.96 (2H, d, J=8Hz, *ortho*); 7.03 (2H, d, J=8Hz, *meta*); 7.52 (30H, m, 2[PPh_3]); 10.20 (1H, br, s, $NHCH_3$); δ_P ($CDCl_3$) −8.10 ppm. *m/z* 1157 ($M - CF_3$); 1093 ($M - CF_3 - SO_2$); 1076 ($M - OSO_2CF_3$); 944 ($1093 - OSO_2CF_3$); 927 ($M - 2OSO_2CF_3$); 600 ($M - 2OSO_2CF_3 - Cl - CO - PPh_3 - H$); 146 (C{$CH_3CH_2C_6H_4$}=NMe).

3.5. *Preparation of· [Ir{C(Me)=NHMe}Cl(OSO_2CF_3) (CO)(PPh_3)$_2$]$^+$[(OSO_2CF_3]$^-$*

Reaction between *N*-methylacetonitrilium triflate (0.06 g, 0.28 mmol) and **3** (0.25 g, 0.27 mmol) gave **2d** (0.15 g, 49%), m.p. 158°C (with decomposition). Anal. Found: C, 43.9; H, 3.4; N, 1.2; S, 5.9. $C_{42}H_{37}ClF_6IrNO_7P_2S_2$ calc., C, 44.4; H, 3.3; N, 1.2; S, 5.9%. $\nu_{max}(CHCl_3)$ 3240w, 3180w, 2080vs, 1605m, 1485m, 1435s, 1340m, (hexadecane) 1280s, 1260s, 1240s, 1205s, 1170s, 1160m, 1090m, 1030s, 995s, 750m, 695s, 630vs cm^{-1}. δ_H ($CDCl_3$) 2.43 (3H, d, $J = 5Hz$, $NHCH_3$); 2 .73 (3H, s, =CCH_3); 7.61 (30H, m, 2[PPh_3]); 9.25 (1H, br, NH); δ_F ($CDCl_3$) 0.44 (s); 2.53 (s); δ_P ($CDCl_3$) −7.32 ppm. *m/z* 986 ($M - OSO_2CF_3$); 837 ($M - 2OSO_2CF_3$); 809 ($M - 2OSO_2CF_3 - CO$); 574 ($M - 2OSO_2CF_3 - PPh_3 - H$); 546 ($M - 2OSO_2CF_3 - PPh_3 - CO - H$).

3.6. *Reaction of [IrCl(CO)(PPh_3)$_2$], triflic acid and N-methylisobutyronitrilium triflate*

Triflic acid (0.10 g, 0.64 mmol, 0.06 cm^3) was added to *N*-methylisobutyronitrilium triflate (0.15 g, 0.63 mmol) dissolved in chloroform (5 cm^3). A solution of Vaska's compound (0.50 g, 0.63 mmol) in the same solvent was transferred by syringe to the solution. The mixture was protected from light and stirred for 30 min. Diethyl ether (30 cm^3) was added until turbidity persisted and the solution was kept at −10°C overnight. The white microcrystals obtained were found to be hydride **3** (0.42 g, 70%).

Acknowledgements

We thank the SERC for the award of a research studentship to A.C.W.

References

1 E. O. Fischer and Maasböl, *Angew. Chem., 76* (1964) 645.

2 D. J. Cardin, B. Cetinkaya and M. F. Lappert, *Chem. Rev., 72* (1972) 545.

3 P. J. Brothers and W. R. Roper, *Adv. Organomet. Chem., 25* (1986) 121.

4 H. Fischer in F. R. Hartley and S. Patai (eds.), *The Chemistry of the Metal–Carbon Bond*, Vol. 1, Wiley–Interscience, New York, 1982, p. 181.

5 E. O. Fischer, P. Stuckler, H. J. Beck and F. R. Kreiszel, *Chem. Ber., 109* (1976) 3089.

6 H. Werner, E. O. Fischer and C. G. Kreiter, *J. Organomet. Chem., 28* (1971) 367.

7 M. F. Lappert and A. J. Oliver, *J. Chem. Soc., Dalton Trans.,* (1974) 65.

8 M. Barber, B. L. Booth, P. J. Bowers and L. Tetler, *J. Organomet. Chem., 328* (1987) C25.

9 B. Olgemöller, H. Bauer, H. Löbermann, U. Nagel and W. Beck, *Chem. Ber., 20* (1981) 470.

10 P. A. Harding and S. D. Robinson, *J. Chem. Soc., Dalton Trans.,* (1987) 947.

11 E. Moser and E. O. Fischer, *J. Organomet. Chem., 16* (1969) 275.

12 G. A. Lawrence, *Chem. Rev., 86* (1986) 17.

13 A. Parlier and H. Rudter, *J. Organomet. Chem., 327* (1987) 339.

14 L. S. Hegedus, L. M. Schultze and J. Montgomery, *Organometallics, 8* (1989) 2189.

15 B. L. Booth, K. O. Jibodu and M. F. J. R. P. Proenca, *J. Chem. Soc., Perkin Trans. 1,* (1983) 1067.

16 P. W. Robinson and A. Wojcicki, *J. Chem. Soc., Chem. Commun.,* (1970) 951.

17 W. L. Jolly, *Inorg. Synth., 11* (1973) 102.