

**FORMATION OF CARBON-CARBON BONDS ON DI(ORGANO)IRIDIUM
 COMPLEXES, $RR' Ir(CO)(PPh_3)_2 X$ ($R, R' = Me, Ph, CH_2Ph, C(O)CH_3$; $X = Cl, I$)
 AND THE CRYSTAL STRUCTURE OF
 $cis, cis, trans-[Ir(CH_3)_2(CO)_2(PPh_3)_2]^+ [CF_3SO_3]^-$**

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Summary

The reactions of RX with $trans-R' Ir(CO)(PPh_3)_2$ are reported. Addition of $CH_3C(O)Cl$ to $trans-CH_3 Ir(CO)(PPh_3)_2$ leads to acetone; addition of CH_3I to $trans-Ph Ir(CO)(PPh_3)_2$ leads to toluene; and addition of CH_3I to $trans-C_6H_5CH_2 Ir(CO)(PPh_3)_2$ leads to ethylbenzene. Reaction of C_2H_5Br with $trans-CH_3 Ir(CO)(PPh_3)_2$ leads to CH_4 and C_2H_4 . The addition of CH_3I to $trans-CH_3 Ir(CO)(PPh_3)_2$ leads to $Ir(CH_3)_2 Ir(CO)(PPh_3)_2 I$ from which $Ir(CH_3)_2(CO)-(PPh_3)_2^+$ and $Ir(CH_3)_2(CO)_2(PPh_3)_2^+$ can be prepared. These dimethyl complexes do not undergo reductive elimination of ethane, acetone or diacetyl under a variety of conditions (CH_4 and C_2H_6 are formed at decomposition). Thus for these complexes the charge, the presence of a free coordination site and the *cis* stereochemistry do not facilitate reductive elimination reactions. To ascertain that no structural features were preventing reductive elimination from the dimethyl complex we have examined the structure of $cis, cis, trans-[Ir(CH_3)_2(CO)_2(PPh_3)_2]^+ [CF_3SO_3]^-$. This crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (C_i^1 ; No. 2) with a 11.708(2), b 11.738(2), c 14.702(2) Å, α 87.544(13), β 79.181(14), γ 76.963(15)°, V 1933.4(6) Å³ and D (calc'd) 1.64 g cm⁻³ for mol. wt. 951.9 and $Z = 2$. X-ray diffraction data ($Mo-K_\alpha$, 2θ 4.5-50.0°) were collected with a Syntex P2₁ automated four-circle diffractometer and the structure was refined to R 3.5% for all 6835 reflections (R 2.9% for those 6133 reflections with $|F_0| > 6\sigma(|F_0|)$). The central d^6 iridium(III) ion has a slightly distorted octahedral stereochemistry, with $Ir-CO$ 1.943(5) and 1.956(5) Å, $Ir-CH_3$ 2.152(5) and 2.155(5) Å and $Ir-PPh_3$ 2.391(1) and 2.400(1) Å; interligand angles include $OC-Ir-CO$ 102.09(20), $CH_3-Ir-CH_3$ 89.70(19) and $PPh_3-Ir-PPh_3$ 174.68(4)°.

Reductive elimination is a reaction of importance in catalytic reactions in removing product from the metal center [1–5]. Despite this importance there have been relatively few studies of bond-forming reactions. Most studies of reductive elimination have centered on C–H bond formation [6–9], although there have been some reports of C–C bond formation [10–12]. Several studies have examined binuclear reductive eliminations [13–18]. In some cases polyalkyl complexes, which do not eliminate alkanes, form ketones in the presence of CO [19–21]. The ready addition of RX to *trans*-Ir(CH₃)(CO)(PPh₃)₂ to give Ir(CH₃)R(CO)(PPh₃)₂X offers the possibility of examining the influence of R on the C–C bond forming reaction.

Similar rhodium complexes have been used to form carbon–carbon bonds between vinyl and methyl groups and between acyl and methyl groups [22,23]. A very recent report described the addition of alkyl halides (Me, Pr, *i*-Pr, etc.) to *trans*-RIr(CO)(PMe₃)₂ [24]. The addition reactions occurred readily, but no carbon–carbon bond-forming elimination reactions occurred from the dialkyliridium(III) complexes. In this manuscript we report that the formation of carbon–carbon bonds depends both on the nature of the alkyl halide and on the nature of the R group on *trans*-RIr(CO)(PPh₃)₂.

Experimental

Iridium trichloride, IrCl₃·*x*H₂O, was loaned by Johnson Matthey, Inc. All solvents were dried and degassed prior to use. All syntheses were accomplished under a nitrogen or argon atmosphere. Infrared spectra were recorded on a Beckman 4240 or a Perkin–Elmer 683 infrared spectrophotometer, and ¹H NMR spectra were recorded on a Varian EM390 or on a JEOL FX90Q. *trans*-MeIr(CO)(PPh₃)₂ and Me₂Ir(CO)(PPh₃)₂I were prepared as previously described [25].

Preparation of [Ir(CH₃)₂(CO)(PPh₃)₂]⁺[CF₃SO₃⁻]

In a dry box, a suspension of 0.40 g Ir(CH₃)₂(CO)(I)(PPh₃)₂ in 20 ml of THF was prepared. To this suspension 0.12 g of CF₃SO₃Ag (1.05 equivalents) were added with stirring, producing a pale yellow solution and light yellow precipitate. The resulting suspension was stirred for 10 minutes, during which time the precipitate darkened. The suspension was filtered (fine fritte) and 40 ml hexanes added to the filtrate, producing a fine white solid which was collected via suction filtration and washed with 2 × 4 ml hexanes, yielding 0.34 g (83%) of air-stable, white, microcrystalline product. Infrared (KBr): 2038(vs), 1996(m). ¹H NMR (CD₂Cl₂): 7.47 ppm(m), 0.73 ppm(t, *J*(P–H) 9 Hz), 0.40 ppm(t, *J*(P–H) 6 Hz). ³¹P{¹H} NMR (CD₂Cl₂, H₃PO₄ external reference): –1.63 ppm(s). The ¹H NMR in DMSO/CH₂Cl₂ shows the two triplets overlapping centered at 0.80 and 0.89 ppm.

Preparation of [Ir(CH₃)₂(CO)₂(PPh₃)₂]⁺[CF₃SO₃⁻]

A solution was prepared in a small Schlenk flask using 0.20 g [Ir(CH₃)₂(CO)-(PPh₃)₂]⁺[CF₃SO₃⁻] and 10 ml of THF. The solution was stirred under an atmosphere of CO for 30 minutes then 12 ml of hexanes were added to the flask to induce precipitation of a white, microcrystalline, air-stable solid which was collected via suction filtration. Yield 0.19 g (92%). Infrared: KBr; 2102(s), 2060(vs) cm⁻¹. CH₂Cl₂; 2098(s), 2054(vs) cm⁻¹. ¹H NMR (CD₂Cl₂); 0.30 ppm(t, *J*(P–H) 6 Hz), 7.60 ppm(m). ³¹P{¹H} (CD₂Cl₂ with external H₃PO₄ reference); –9.18 ppm(s).

Preparation of trans-PhIr(CO)(PPh₃)₂

In an inert atmosphere glove box an excess of PhLi was added to a suspension of *trans*-Ir(CO)(PPh₃)₂Cl in THF. After the mixture was stirred for 1 hour, florasil was added to react with excess PhLi and the filtrate was collected. The THF was removed and the solid was recrystallized from benzene/hexanes. The infrared spectrum (1942 cm⁻¹) is in agreement with that previously recorded [26].

Addition of RX to trans-R'Ir(CO)(PPh₃)₂

In general *trans*-R'Ir(CO)(PPh₃)₂ was placed in a vacuum vessel and removed from an inert atmosphere glove box. On a vacuum line the appropriate solvent and RX were distilled into the vessel. The reaction was allowed to proceed several hours before the gas, liquid and solid were examined by chromatography and spectroscopy.

Crystallization of [Ir(CH₃)₂(CO)₂(PPh₃)₂]⁺[CF₃SO₃⁻]

Method A. In a dry box, 10 ml of a saturated solution of [Ir(CH₃)₂(CO)(PPh₃)₂]⁺[CF₃SO₃⁻] in THF were prepared in a Schlenk flask. The flask was sealed and brought out of the dry box where CO was introduced with stirring (20 min). The resulting solution was filtered and transferred to a vapor diffusion crystallization apparatus which was charged with pentane and sealed under an atmosphere of CO. The apparatus was allowed to stand for 4 days resulting in precipitation of needle-shaped, white crystals. The mother liquor was removed from the apparatus and the crystals washed with pentane and dried under a stream of N₂. The crystals were too thin for single crystal X-ray diffraction analysis but were suitable for microanalysis. Analysis: Found: C, 51.72; H, 3.81; P, 6.42; F, 5.99. C₄₁H₃₆F₃IrO₅P₂S calcd.: C, 51.72; H, 3.78; P, 6.52; F, 5.99%. The infrared and ¹H NMR are identical to that obtained for a sample of microcrystalline product.

Method B. A procedure identical to that in method A is followed, except CH₂Cl₂ is utilized as the solvent and the entire preparation carried out under N₂ outside of a dry box. Crystals suitable for single crystal X-ray diffraction result by this method.

Observations on the thermal stability of [Ir(CH₃)₂(CO)(PPh₃)₂]⁺[CF₃SO₃⁻]

An NMR tube containing [Ir(CH₃)₂(CO)(PPh₃)₂]⁺[CF₃SO₃⁻] dissolved in CD₂Cl₂ was prepared (CH₂Cl₂ reference), sealed, heated in a 50°C oil bath with occasional monitoring of the samples via ¹H NMR. The resulting spectra revealed no observable decomposition of the complex over a 24 h period at 40–50°C. After completion of the experiment the NMR tube was opened, the solution withdrawn, placed in a small flask, and evaporated to dryness via a stream of N₂. The resulting solid was dissolved in CH₂Cl₂ and CO bubbled through the solution. An infrared of the solution revealed absorbances at 2098(s) and 2052(vs) cm⁻¹ attributable to [Ir(CH₃)₂(CO)₂(PPh₃)₂]⁺[CF₃SO₃⁻]

Collection of the X-ray diffraction data for [Ir(CH₃)₂(CO)₂(PPh₃)₂]⁺[CF₃SO₃⁻]

The crystal selected for the structural analysis was a well-formed parallelepiped with approximate orthogonal dimensions of 0.3 × 0.3 × 0.5 mm³. It was sealed into a thin-walled capillary and mounted on our Syntex P2₁ automated four-circle diffractometer with its extended direction approximately coincident with the φ-axis.

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+ [\text{CF}_3\text{SO}_3]^-$

| | |
|---|---|
| <i>(A) Unit cell data</i> | |
| a 11.708(2) Å | crystal system: triclinic |
| b 11.738(2) Å | space group: $P\bar{1}$ (C_i^1 ; No. 2) |
| c 14.702(2) Å | $Z = 2$ |
| α 87.544(13)° | formula: $\text{C}_{41}\text{H}_{36}\text{F}_3\text{IrO}_5\text{P}_2\text{S}$ |
| β 79.181(14)° | mol. wt. 951.9 |
| γ 76.963(15)° | $D(\text{calc'd})$ 1.64 g/cm ³ |
| V 1933.35(59) Å ³ | T 24° C (297 K) |
| <i>(B) Collection of X-ray diffraction data</i> | |
| Diffractometer: Syntex P2 ₁ | |
| Radiation: Mo- K_α (λ 0.710730 Å) | |
| Monochromator: highly orientated (pyrolytic) graphite; equatorial mode with $2\theta(\text{m})$ 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction. | |
| Reflections meas'd: $+h, \pm k, \pm l$ for 2θ : 4.5° → 50°; yielding 6835 unique data. | |
| Scan type: coupled $\theta(\text{crystal}) - 2\theta(\text{counter})$ | |
| Scan width: $[2\theta(K_{\alpha_1}) - 1.0]^\circ \rightarrow [2\theta(K_{\alpha_2}) + 1.0]^\circ$ | |
| Scan speed: 3.50 deg/min (2θ) | |
| Backgrounds: stationary-crystal, stationary-counter at the two extremes of the 2θ scan; each for one-quarter of the total scan time. | |
| Standard reflections: three mutually orthogonal reflections collected before each set of 97 data points. No decay observed. | |
| Absorption correction: $\mu(\text{Mo-}K_\alpha)$ 38.6 cm ⁻¹ ; corrected empirially by interpolation (in 2θ and ϕ) between 6 close-to-axial (ψ -scan) reflections. | |

Subsequent set-up operations (determination of the crystal's orientation matrix and accurate cell dimensions) and data collection were carried out as described previously [27]; details appear in Table 1. The diffraction symmetry (C_i ; $\bar{1}$) and lack of systematic absences indicate that the crystal belongs to the triclinic system. Possible space groups are the non-centrosymmetric $P1$ (C_1^1 ; No. 1) or the centrosymmetric $P\bar{1}$ (C_i^1 ; No. 2). The latter, centrosymmetric, possibility is strongly indicated by the number of molecules per unit cell ($Z = 2$) and by intensity statistics and is confirmed by the successful solution of the structure in this higher symmetry space group.

All data were corrected for the effects of absorption and for Lorentz and polarization factors. Symmetry-equivalent reflections were averaged ($R(I)$ 2.2% for 369 pairs). Data were converted to unscaled $|F_0|$ values; any reflection with $I < 0$ was assigned the value $|F_0| = 0$. Data were placed on an approximately absolute scale by means of a Wilson plot, which also provided the average overall isotropic thermal parameter, $\bar{B} = 2.33 \text{ \AA}^2$.

Solution and refinement of the structure

All subsequent calculations were performed using our locally-modified version of the Syntex XTL interactive crystallographic program package [28]. The structure was solved by means of a Patterson map which revealed the location of the iridium atom. All remaining non-hydrogen atoms were located from a difference-Fourier map. Five of the six methyl hydrogens were located from a subsequent difference-

TABLE 2

FINAL POSITIONAL PARAMETERS FOR $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+ [\text{CF}_3\text{SO}_3^-]$

| Atom | x | y | z | B (Å ²) |
|-------|--------------|--------------|--------------|---------------------|
| Ir | 0.23803(1) | 0.19705(1) | 0.22668(1) | |
| P(1) | 0.44762(10) | 0.15735(10) | 0.22639(8) | |
| P(2) | 0.03077(9) | 0.21953(9) | 0.22028(7) | |
| C(1) | 0.19582(41) | 0.28394(44) | 0.34322(33) | |
| O(1) | 0.16612(37) | 0.32174(41) | 0.41497(26) | |
| C(2) | 0.25450(40) | 0.32016(41) | 0.13572(33) | |
| O(2) | 0.26581(35) | 0.38859(33) | 0.08061(27) | |
| C(3) | 0.22808(43) | 0.05517(46) | 0.32369(34) | |
| C(4) | 0.27249(40) | 0.07564(41) | 0.11398(32) | |
| C(11) | 0.54036(40) | 0.01010(39) | 0.19955(30) | 3.144(78) |
| C(12) | 0.66190(49) | -0.00021(48) | 0.16805(38) | 4.38(10) |
| C(13) | 0.73811(54) | -0.10781(52) | 0.14984(40) | 4.96(11) |
| C(14) | 0.69392(53) | -0.20745(51) | 0.16343(40) | 4.90(11) |
| C(15) | 0.57459(52) | -0.20043(49) | 0.19579(39) | 4.69(11) |
| C(16) | 0.49672(46) | -0.09175(45) | 0.21338(35) | 4.025(94) |
| C(21) | 0.52085(39) | 0.24473(37) | 0.13738(29) | 2.901(74) |
| C(22) | 0.55703(45) | 0.34398(43) | 0.15599(34) | 3.854(91) |
| C(23) | 0.60743(53) | 0.40687(51) | 0.08458(40) | 4.96(11) |
| C(24) | 0.62168(51) | 0.37339(50) | -0.00595(39) | 4.72(11) |
| C(25) | 0.58585(49) | 0.27489(48) | -0.02523(37) | 4.36(10) |
| C(26) | 0.53552(46) | 0.21091(44) | 0.04517(34) | 3.929(93) |
| C(31) | 0.48104(42) | 0.19252(40) | 0.33751(31) | 3.335(81) |
| C(32) | 0.44141(47) | 0.30566(45) | 0.37208(35) | 4.12(10) |
| C(33) | 0.46256(56) | 0.33220(53) | 0.45787(42) | 5.34(12) |
| C(34) | 0.51927(62) | 0.24694(61) | 0.50897(47) | 6.09(14) |
| C(35) | 0.55843(63) | 0.13463(62) | 0.47692(47) | 6.16(14) |
| C(36) | 0.53991(50) | 0.10599(48) | 0.39012(38) | 4.57(10) |
| C(41) | -0.00734(40) | 0.22265(38) | 0.10416(30) | 3.062(77) |
| C(42) | 0.01655(50) | 0.31194(48) | 0.04550(37) | 4.45(10) |
| C(43) | -0.01931(55) | 0.32498(53) | -0.04119(42) | 5.29(12) |
| C(44) | -0.08226(56) | 0.24814(55) | -0.06556(43) | 5.32(12) |
| C(45) | -0.10643(56) | 0.16064(54) | -0.00769(42) | 5.30(12) |
| C(46) | -0.07093(47) | 0.14629(45) | 0.07777(35) | 4.12(10) |
| C(51) | -0.06785(39) | 0.35775(37) | 0.26540(29) | 2.958(75) |
| C(52) | -0.19079(46) | 0.36917(44) | 0.27839(34) | 3.894(91) |
| C(53) | -0.26804(52) | 0.47403(50) | 0.30731(39) | 4.71(11) |
| C(54) | -0.22350(53) | 0.56804(51) | 0.32443(39) | 4.87(11) |
| C(55) | -0.10319(53) | 0.55890(50) | 0.31007(40) | 4.88(11) |
| C(56) | -0.02414(45) | 0.45418(44) | 0.28035(34) | 3.846(91) |
| C(61) | -0.03000(38) | 0.10550(36) | 0.28529(28) | 2.762(72) |
| C(62) | 0.00180(45) | -0.00947(43) | 0.25238(33) | 3.759(89) |
| C(63) | -0.03612(51) | -0.09838(49) | 0.30610(39) | 4.64(11) |
| C(64) | -0.10072(55) | -0.07576(53) | 0.39337(42) | 5.24(12) |
| C(65) | -0.12778(52) | 0.03663(51) | 0.42850(40) | 4.88(11) |
| C(66) | -0.09311(44) | 0.12607(42) | 0.37506(33) | 3.708(88) |
| S | 0.28927(13) | 0.62292(12) | 0.28539(9) | |
| O(4) | 0.41143(37) | 0.59861(40) | 0.29645(31) | |
| O(5) | 0.24989(46) | 0.72883(44) | 0.23812(31) | |
| O(6) | 0.25353(46) | 0.52338(45) | 0.25912(33) | |
| C(5) | 0.20884(55) | 0.64929(57) | 0.40281(39) | |
| F(1) | 0.09291(37) | 0.66584(49) | 0.40952(31) | |
| F(2) | 0.22421(50) | 0.74720(45) | 0.43420(32) | |
| F(3) | 0.24001(54) | 0.56716(54) | 0.45866(30) | |

continued

TABLE 2 (continued)

| Atom | x | y | z | B (Å ²) |
|-------|---------|---------|---------|---------------------|
| H(3A) | 0.1618 | 0.0779 | 0.3767 | 6.0 |
| H(3B) | 0.3012 | 0.0407 | 0.3516 | 6.0 |
| H(3C) | 0.2403 | -0.0079 | 0.2907 | 6.0 |
| H(4A) | 0.3525 | 0.0589 | 0.0966 | 6.0 |
| H(4B) | 0.2304 | 0.1237 | 0.0672 | 6.0 |
| H(4C) | 0.2481 | 0.0016 | 0.1186 | 6.0 |
| H(12) | 0.6928 | 0.0684 | 0.1588 | 6.0 |
| H(13) | 0.8209 | -0.1132 | 0.1281 | 6.0 |
| H(14) | 0.7461 | -0.2817 | 0.1501 | 6.0 |
| H(15) | 0.5451 | -0.2698 | 0.2062 | 6.0 |
| H(16) | 0.4141 | -0.0869 | 0.2348 | 6.0 |
| H(22) | 0.5470 | 0.3690 | 0.2180 | 6.0 |
| H(23) | 0.6324 | 0.4747 | 0.0981 | 6.0 |
| H(24) | 0.6562 | 0.4177 | -0.0547 | 6.0 |
| H(25) | 0.5954 | 0.2508 | -0.0876 | 6.0 |
| H(26) | 0.5108 | 0.1428 | 0.0310 | 6.0 |
| H(32) | 0.3996 | 0.3653 | 0.3368 | 6.0 |
| H(33) | 0.4371 | 0.4101 | 0.4806 | 6.0 |
| H(34) | 0.5320 | 0.2652 | 0.5682 | 6.0 |
| H(35) | 0.5982 | 0.0757 | 0.5134 | 6.0 |
| H(36) | 0.5677 | 0.0280 | 0.3675 | 6.0 |
| H(42) | 0.0578 | 0.3656 | 0.0636 | 6.0 |
| H(43) | -0.0002 | 0.3856 | -0.0825 | 6.0 |
| H(44) | -0.1088 | 0.2569 | -0.1233 | 6.0 |
| H(45) | -0.1484 | 0.1074 | -0.0258 | 6.0 |
| H(46) | -0.0896 | 0.0849 | 0.1180 | 6.0 |
| H(52) | -0.2219 | 0.3041 | 0.2668 | 6.0 |
| H(53) | -0.3517 | 0.4807 | 0.3156 | 6.0 |
| H(54) | -0.2765 | 0.6395 | 0.3460 | 6.0 |
| H(55) | -0.0726 | 0.6249 | 0.3205 | 6.0 |
| H(56) | 0.0596 | 0.4487 | 0.2703 | 6.0 |
| H(62) | 0.0494 | -0.0267 | 0.1926 | 6.0 |
| H(63) | -0.0167 | -0.1756 | 0.2822 | 6.0 |
| H(64) | -0.1273 | -0.1368 | 0.4298 | 6.0 |
| H(65) | -0.1705 | 0.0520 | 0.4899 | 6.0 |
| H(66) | -0.1124 | 0.2028 | 0.3999 | 6.0 |

Fourier map; the position of the sixth was calculated as were the positions of all hydrogen atoms associated with phenyl rings of the PPh₃ ligands; a carbon-hydrogen distance of 0.95 Å was assumed [29]. Positions of these hydrogen atoms were up-dated, but were not refined. The structure was optimized by full-matrix least-squares refinement of the residual $\sum w(|F_0| - |F_c|)^2$, where $w = \{[\sigma(|F_0|)]^2 + [0.015|F_0|]^2\}^{-1}$. Anisotropic thermal parameters were used for atoms in the Ir(C)₂(CO)₂(P)₂ core of the cation and for all atoms of the CF₃SO₃⁻ anion; isotropic thermal parameters were used for carbon atoms of the phenyl rings. Final convergence was reached with [30] R_F 3.5%, R_{wF} 3.8% and GOF 1.74 for all 6835 reflections (R_F 3.1%, R_{wF} 3.7% for those 6397 reflections with $|F_0| > 3\sigma(|F_0|)$; R_F 2.9%, R_{wF} 3.7% for those 6133 reflections with $|F_0| > 6\sigma(|F_0|)$). A final difference-Fourier map was "clean", the maximum feature being a peak of height 0.46 e⁻ Å⁻³ in the immediate vicinity of the iridium atom; the structure is thus

TABLE 3

ANISOTROPIC THERMAL PARAMETERS ^a FOR [Ir(CH₃)₂(CO)₂(PPh₃)₂]⁺ [CF₃SO₃⁻]

| Atom | B ₁₁ | B ₂₂ | B ₃₃ | B ₁₂ | B ₁₃ | B ₂₃ |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Ir | 2.0578(76) | 2.5492(77) | 2.3623(74) | -0.7424(49) | -0.4555(47) | 0.0785(47) |
| P(1) | 2.188(44) | 2.914(45) | 2.961(45) | -0.804(35) | -0.523(35) | 0.177(35) |
| P(2) | 2.219(43) | 2.550(42) | 2.664(43) | -0.695(34) | -0.437(34) | -0.081(33) |
| C(1) | 2.75(20) | 4.65(24) | 3.38(21) | -1.10(17) | -0.44(16) | -0.63(18) |
| O(1) | 5.18(21) | 8.46(27) | 3.70(18) | -1.36(19) | -0.07(15) | -2.10(17) |
| C(2) | 2.82(20) | 3.30(20) | 3.73(21) | -0.78(16) | -0.77(16) | 0.12(17) |
| O(2) | 5.14(20) | 4.80(18) | 5.51(20) | -1.92(15) | -1.46(16) | 2.39(16) |
| C(3) | 3.09(21) | 4.64(24) | 3.78(22) | -1.18(18) | -0.74(17) | 1.45(18) |
| C(4) | 2.72(19) | 3.69(21) | 3.41(20) | -0.37(16) | -0.72(15) | -0.73(16) |
| S | 4.652(65) | 4.437(60) | 3.449(53) | -1.590(50) | -0.279(46) | -0.466(44) |
| O(4) | 4.36(20) | 7.18(25) | 6.98(25) | -1.52(18) | -0.28(17) | -1.03(20) |
| O(5) | 8.82(32) | 7.04(26) | 5.39(23) | -0.26(22) | -0.28(21) | 1.94(19) |
| O(6) | 8.25(31) | 8.37(30) | 7.03(26) | -4.55(25) | 0.18(22) | -3.14(23) |
| C(5) | 4.91(31) | 6.16(32) | 4.04(26) | -1.06(24) | -0.65(22) | -0.80(23) |
| F(1) | 4.83(21) | 13.61(37) | 7.81(25) | -1.18(22) | 0.94(18) | 0.27(24) |
| F(2) | 12.40(37) | 10.65(32) | 8.05(27) | -3.79(28) | 0.70(24) | -5.74(25) |
| F(3) | 12.86(40) | 14.53(43) | 5.06(21) | 2.94(32) | 0.92(23) | 4.03(25) |

^a Anisotropic thermal parameters are in standard XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)]$.

both correct and complete. Final positional and thermal parameters are collected in Tables 2 and 3.

Throughout the analysis, the values of F_c were based upon the analytical expressions for the neutral atoms' form factors; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms [31].

Results and discussion

The addition of a variety of RX compounds to *trans*-R'Ir(CO)(PPh₃)₂ occurs readily, with the nature of the products depending on R and R'.



Reaction of CH₃C(O)Cl with *trans*-CH₃Ir(CO)(PPh₃)₂ leads to acetone (95%) [32] and HIr(CO)(PPh₃)₂Cl₂ [33]. Products from the reactions with acetyl chloride are quite susceptible to hydrolysis to the hydride product [34]. Addition of C₂H₅Br to *trans*-CH₃Ir(CO)(PPh₃)₂ leads to *trans*-Ir(CO)(PPh₃)₂Br (1954 cm⁻¹) and CH₄, C₂H₄ and C₂H₆ with no trace of propane. Thus β-elimination from the ethyl complex is a more rapid process than carbon-carbon bond formation between CH₃ and C₂H₅ fragments. The mechanism of this β-elimination reaction will be the subject of future study. Reaction of CH₃I with *trans*-PhIr(CO)(PPh₃)₂ leads to toluene and *trans*-Ir(CO)(PPh₃)₂I (1957 cm⁻¹). Similarly reaction of *trans*-C₆H₅-CH₂Ir(CO)(PPh₃)₂ with MeI leads to ethyl benzene [36]. Thus for every case except R = R' = CH₃, reaction of RX with *trans*-R'Ir(CO)(PPh₃) results in oxidative addition followed by a reductive elimination reaction that usually involves C-C bond formation.

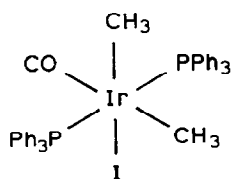


Fig. 1. Coordination geometry of $\text{Ir}(\text{CH}_3)_2(\text{I})(\text{CO})(\text{PPh}_3)_2$.

Rapid oxidative addition of CH_3I to *trans*- $\text{Ir}(\text{CH}_3)(\text{CO})(\text{PPh}_3)_2$ occurs in benzene, utilizing only a slight excess (1.1 equivalents) of CH_3I [25]. An ^1H NMR spectrum of the dimethyliridium(III) complex reveals the methyl groups to be inequivalent and coupled to equivalent phosphine ligands. Such observations are consistent with *trans* addition of CH_3I , producing a *cis*-dimethyl complex as illustrated in Fig. 1. A *trans* stereochemistry for addition of MeI is in agreement with that previously demonstrated for the addition of methyl halides to unsaturated transition metal complexes [37].

The compound $\text{Ir}(\text{CH}_3)_2(\text{I})(\text{CO})(\text{PPh}_3)_2$ is thermally stable below 80°C . Slow decomposition occurs at 90°C and becomes rapid at 110°C . Photochemical decomposition is achieved by irradiation at room temperature for a short period of time. In either case, the product distribution is similar, with formation of CH_4 as the predominant species along with minor amounts of C_2H_4 and C_2H_6 , as ascertained via gas chromatographic analysis of the gas phase of the reaction mixture. Apparently, the reductive elimination of the *cis*-methyl ligands to form C_2H_6 does not occur readily. The decomposition may progress via $\text{Ir}-\text{CH}_3$ bond cleavage and/or α -hydride abstraction (following ligand dissociation). Similar reactivity has been reported for a stable dialkyliridium(III) complex, $\text{Ir}(\text{CH}_3)(\text{R})[\text{N}(\text{Si}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2)_2]$, where $\text{R} = \text{CH}_2\text{C}(\text{CH}_3)_3$ or $\text{CH}_2\text{Si}(\text{CH}_3)_3$ [38]. Both complexes are thermally stable at temperatures above 80°C for extended periods of time. Where $\text{R} = \text{CH}_2\text{C}(\text{CH}_3)_3$, photo-induced α -hydrogen elimination is documented to occur, forming $\text{H}_2\text{Ir}[\text{N}(\text{Si}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2)_2]$ and *t*-butylethylene (55%) as well as $\text{CH}_2\text{Ir}[\text{N}(\text{Si}(\text{CH}_3)_2\text{CH}_2\text{PPh}_2)_2]$ and neopentane (45%).

In an effort to facilitate reductive elimination of C_2H_6 from the complex, abstraction of the iodide of $\text{Ir}(\text{CH}_3)_2(\text{I})(\text{CO})(\text{PPh}_3)_2$ was carried out using $\text{CF}_3\text{SO}_3\text{Ag}$. Instead, a remarkably stable cationic complex, $[\text{Ir}(\text{CH}_3)_2(\text{CO})(\text{PPh}_3)_2]^+[\text{CF}_3\text{SO}_3^-]$, was produced. The coordination geometry inferred from ^1H and ^{31}P NMR spectral data (^1H : two methyl triplets of equal intensity, shift values solvent dependent, $^{31}\text{P}\{^1\text{H}\}$: single sharp resonance) is consistent with *cis*-methyl groups, *trans*-phosphine ligands and a sixth coordination site occupied by solvent [39]. With a *cis* stereochemistry for the methyl groups, an open coordination site and a cationic complex one would anticipate rapid reductive elimination of ethane [37]. Observation of methylene chloride solutions of $[\text{Ir}(\text{CH}_3)_2(\text{CO})(\text{PPh}_3)_2]^+[\text{CF}_3\text{SO}_3^-]$ via ^1H NMR reveals the cationic complex to be stable with respect to decomposition, even at temperatures of 40 – 50°C for extended periods of time (24 h). At 90°C in DME formation of roughly equal quantities of CH_4 and C_2H_6 is observed over a period of 48 h.

Exposure of solutions containing $[\text{Ir}(\text{CH}_3)_2(\text{CO})(\text{PPh}_3)_2]^+[\text{CF}_3\text{SO}_3^-]$ to CO results in the displacement of solvent from the coordination sphere of iridium and

the subsequent formation of a dicarbonyl species, $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+[\text{CF}_3\text{SO}_3^-]$. Infrared and NMR (^1H , ^{31}P) spectra as well as elemental analysis (C,H,P,F) are consistent with the suggested formulation. Infrared and NMR (^1H , ^{31}P) spectra also indicate a hexacoordinate geometry consisting of *cis*-methyl ligands and *trans*-phosphine ligands, with remaining CO ligands also *cis*. Since the complex is stable to reductive elimination of ethane, acetone and diacetyl below 80°C , we undertook a single crystal X-ray diffraction analysis to ascertain the geometry.

Description of the molecular structure of $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+[\text{CF}_3\text{SO}_3^-]$

The crystal contains an ordered arrangement of $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+$ cations and $[\text{CF}_3\text{SO}_3^-]$ anions in a 1/1 ratio. The ions are separated by normal Van der Waals' distances; there are no abnormally short interionic contacts. The overall geometry of the $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+$ cation and the atomic labeling scheme for this moiety are depicted in Fig. 2, while Fig. 3 provides a stereoscopic view of this cation. Interatomic distances and angles are collected in Tables 4 and 5.

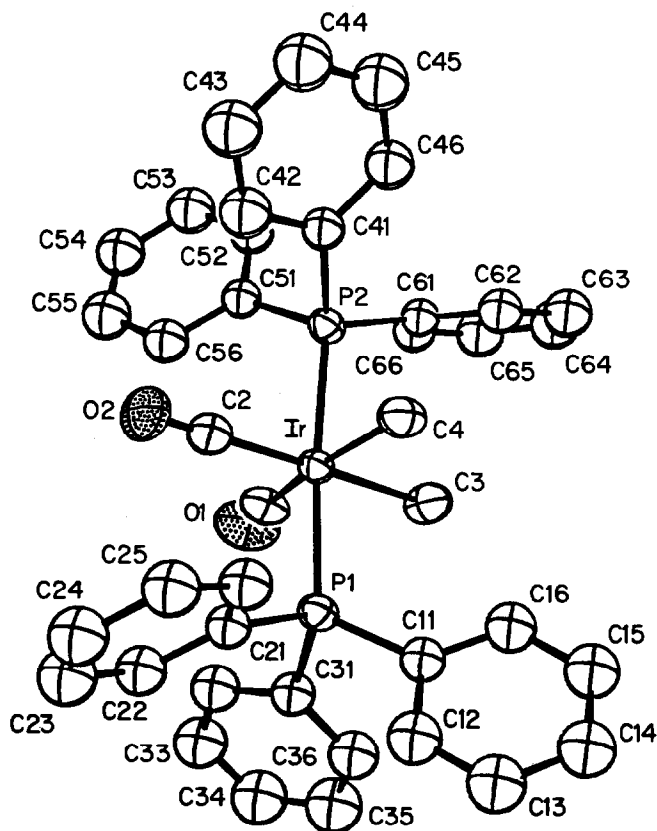


Fig. 2. Stereochemistry and labeling of non-hydrogen atoms in the $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+$ cation. (ORTEP-II diagrams, 30% ellipsoids.) Note that carbon atoms of the phenyl rings were refined isotropically and are thus represented by spheres.

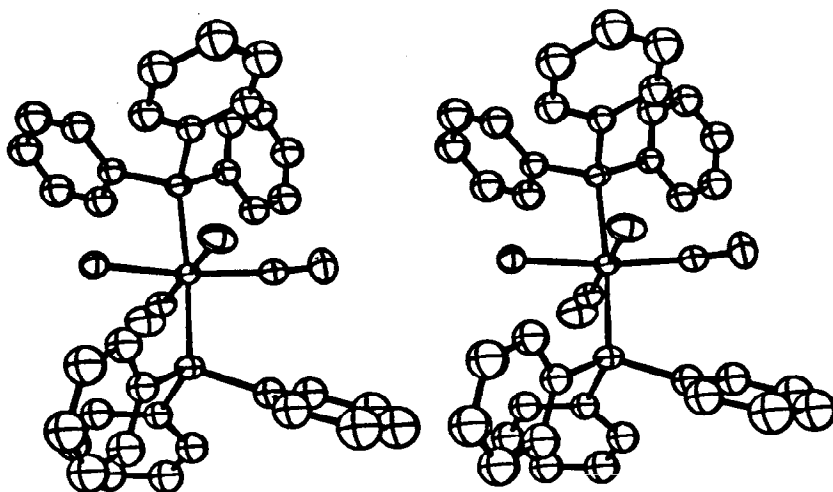


Fig. 3. Stereoscopic view of the $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+$ cation.

The cation contains a central d^6 iridium(III) ion in a slightly distorted octahedral stereochemical environment. The structural study confirms that the isomer produced is the *cis*-dimethyl-*cis*-dicarbonyl-*trans*-bis(triphenylphosphine)iridium(III) cation. Figure 4 depicts all possible isomers of $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+$ in structures 1–4 and 5a and 5b. The observed isomer, 2 would appear to be the thermodynamically most stable, with σ -donor methyl groups *trans* to π -acceptor carbonyls and with the bulky phosphine ligands in mutually *trans* sites.

The *trans* angles in the coordination sphere are, in increasing order, C(1)–Ir–C(4) 169.17(19), P(1)–Ir–P(2) 174.68(4) and C(2)–Ir–C(3) 177.07(20)°. Most of the *cis* angles lie within 4° of the ideal value of 90° (specifically in the range 86.23(13)–93.96(15)°); the two exceptions to this are: (a) the angle between the two carbonyl ligands, C(1)–Ir–C(2), which is increased to a value of 102.09(20)°; (b) the OC–Ir–CH₃ angle defined by C(1)–Ir–C(3), which is decreased to a value of 79.99(20)°.

The iridium-carbonyl systems are associated with bond angles of Ir–C(1)–O(1) 171.0(5)° (bent, possibly, due to interaction with C(3), *vide supra*) and Ir–C(2)–O(2) 177.5(4)°. The Ir–CO distances are Ir–C(1) 1.956(5) and Ir–C(2) 1.943(5) Å (average 1.950 ± 0.010 Å, while C–O distances are C(1)–O(1) 1.124(6) and C(2)–O(2) 1.127(6) Å (average 1.126 ± 0.002 Å).

The mutually *cis* methyl ligands define the interligand angle C(3)–Ir–C(4) 89.70(19)° and are associated with bond lengths of Ir–C(3) 2.155(5) and Ir–C(4) 2.152(5) Å, averaging 2.154 ± 0.002 Å; a value some 0.20 Å longer than the average Ir–CO distance but in the normal range for alkyliridium(III) linkages; there is, therefore, nothing anomalous in the iridium–methyl bonding.

Formation of carbon–carbon bonds by reductive elimination from a metal center is a process that remains poorly understood [37]. While C₂H₆ can be eliminated from some dimethyl complexes [10a,12,40], other dimethyl complexes are stable towards reductive elimination [41]. Several dimethyl complexes which do not eliminate C₂H₆, react with CO to form acetone [19–21]. These iridium complexes also show the facility for elimination of acetone (from an acetyl and methyl) in

TABLE 4. INTERATOMIC DISTANCES (Å) FOR $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+ [\text{CF}_3\text{SO}_3^-]$

| | | | |
|---|-----------|-------------|----------|
| <i>(A) Iridium–Ligand distances</i> | | | |
| Ir–P(1) | 2.391(1) | Ir–C(2) | 1.943(5) |
| Ir–P(2) | 2.400(1) | Ir–C(3) | 2.155(5) |
| Ir–C(1) | 1.956(5) | Ir–C(4) | 2.152(5) |
| <i>(B) Phosphorus–Carbon distances</i> | | | |
| P(1)–C(11) | 1.837(5) | P(2)–C(41) | 1.841(5) |
| P(1)–C(21) | 1.833(4) | P(2)–C(51) | 1.834(4) |
| P(1)–C(31) | 1.834(5) | P(2)–C(61) | 1.810(4) |
| <i>(C) Carbon–Oxygen distances</i> | | | |
| C(1)–O(1) | 1.124(6) | C(2)–O(2) | 1.127(6) |
| <i>(D) Carbon–Carbon distances</i> | | | |
| C(11)–C(12) | 1.391(8) | C(21)–C(22) | 1.380(7) |
| C(12)–C(13) | 1.376(8) | C(22)–C(23) | 1.376(8) |
| C(13)–C(14) | 1.375(9) | C(23)–C(24) | 1.373(8) |
| C(14)–C(15) | 1.374(9) | C(24)–C(25) | 1.373(8) |
| C(15)–C(16) | 1.393(8) | C(25)–C(26) | 1.373(7) |
| C(16)–C(11) | 1.396(7) | C(26)–C(21) | 1.397(6) |
| C(31)–C(32) | 1.389(7) | C(41)–C(42) | 1.373(7) |
| C(32)–C(33) | 1.391(8) | C(42)–C(43) | 1.407(8) |
| C(33)–C(34) | 1.353(9) | C(43)–C(44) | 1.383(9) |
| C(34)–C(35) | 1.367(10) | C(44)–C(45) | 1.351(9) |
| C(35)–C(36) | 1.401(9) | C(45)–C(46) | 1.388(8) |
| C(36)–C(31) | 1.386(7) | C(46)–C(41) | 1.396(7) |
| C(51)–C(52) | 1.392(7) | C(61)–C(62) | 1.398(6) |
| C(52)–C(53) | 1.383(8) | C(62)–C(63) | 1.384(8) |
| C(53)–C(54) | 1.373(8) | C(63)–C(64) | 1.365(8) |
| C(54)–C(55) | 1.365(9) | C(64)–C(65) | 1.384(8) |
| C(55)–C(56) | 1.393(8) | C(65)–C(66) | 1.373(8) |
| C(56)–C(51) | 1.384(7) | C(66)–C(61) | 1.388(6) |
| <i>(E) Distances within CF_3SO_3^- anion</i> | | | |
| C(5)–F(1) | 1.312(8) | S–O(4) | 1.433(5) |
| C(5)–F(2) | 1.318(8) | S–O(5) | 1.424(5) |
| C(5)–F(3) | 1.274(8) | S–O(6) | 1.418(5) |
| S–C(5) | 1.807(6) | | |

comparison to ethane. The conditions for the reactions suggest that formation of the carbon–carbon bond, by combination between an acyl and a methyl, occurs greater than three orders of magnitude more rapidly than from two methyl groups. Our data also suggest that formation of an aryl–carbon bond and a benzyl–carbon bond occurs more readily than formation of C_2H_6 from two methyl groups. Thus there appears to be unusual stability to these dimethyliridium complexes.

The reason for the failure to reductively eliminate C_2H_6 or acetone from $\text{Ir}(\text{CH}_3)_2(\text{I})(\text{CO})(\text{PPh}_3)_2$ and $[\text{Ir}(\text{CH}_3)_2(\text{CO})(\text{PPh}_3)_2]^+ [\text{CF}_3\text{SO}_3^-]$ is not obvious. Using phosphine ligands of good σ -donor ability and small size has commonly been employed to impart stability to high oxidation state complexes containing *cis*-dialkyl or *cis*-hydrido, alkyl ligands [10,12,16,19]. However, PPh_3 is neither a “good” σ -donor nor a “small” phosphine ligand. Previous reports have shown that oxidation of the central metal atom facilitates reductive elimination reactions involving *cis*-dialkyl or *cis*-hydrido, alkyl complexes [10a,42–49], yet transformation of $\text{Ir}(\text{CH}_3)_2(\text{I})(\text{CO})(\text{PPh}_3)_2$ to its cationic derivative $[\text{Ir}(\text{CH}_3)_2(\text{CO})(\text{PPh}_3)_2]^+$ -

TABLE 5

INTERATOMIC ANGLES (in Deg.) FOR $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+ [\text{CF}_3\text{SO}_3^-]$

| | | | |
|---|------------|-------------------|------------|
| <i>(A) Angles about the iridium atom</i> | | | |
| P(1)–Ir–P(2) | 174.68(4) | P(2)–Ir–C(1) | 90.45(15) |
| P(1)–Ir–C(1) | 93.96(15) | P(2)–Ir–C(2) | 91.91(14) |
| P(1)–Ir–C(2) | 90.06(14) | P(2)–Ir–C(3) | 90.12(14) |
| P(1)–Ir–C(3) | 87.74(14) | P(2)–Ir–C(4) | 86.23(13) |
| P(1)–Ir–C(4) | 88.89(13) | C(1)–Ir–C(2) | 102.09(20) |
| C(2)–Ir–C(3) | 177.07(20) | C(1)–Ir–C(3) | 79.99(20) |
| C(2)–Ir–C(4) | 88.33(19) | C(1)–Ir–C(4) | 169.17(19) |
| C(3)–Ir–C(4) | 89.70(19) | | |
| <i>(B) Ir–P–C and C–P–C angles</i> | | | |
| Ir–P(1)–C(11) | 120.46(15) | C(11)–P(1)–C(21) | 101.29(21) |
| Ir–P(1)–C(21) | 110.45(15) | C(11)–P(1)–C(31) | 103.89(21) |
| Ir–P(1)–C(31) | 112.35(16) | C(21)–P(1)–C(31) | 107.18(21) |
| Ir–P(2)–C(41) | 116.51(15) | C(41)–P(2)–C(51) | 99.10(20) |
| Ir–P(2)–C(51) | 116.00(15) | C(41)–P(2)–C(61) | 107.23(20) |
| Ir–P(2)–C(61) | 111.15(14) | C(51)–P(2)–C(61) | 105.64(20) |
| <i>(C) Ir–C–O angles</i> | | | |
| Ir–C(1)–O(1) | 171.04(45) | Ir–C(2)–O(2) | 177.54(43) |
| <i>(D) P–C–C angles</i> | | | |
| P(1)–C(11)–C(12) | 117.75(37) | P(2)–C(41)–C(42) | 118.02(37) |
| P(1)–C(11)–C(16) | 123.70(37) | P(2)–C(41)–C(46) | 122.55(36) |
| P(1)–C(21)–C(22) | 123.87(36) | P(2)–C(51)–C(52) | 119.07(35) |
| P(1)–C(21)–C(26) | 117.41(35) | P(2)–C(51)–C(56) | 122.04(35) |
| P(1)–C(31)–C(32) | 119.87(37) | P(2)–C(61)–C(62) | 120.57(34) |
| P(1)–C(31)–C(36) | 120.73(38) | P(2)–C(61)–C(66) | 120.46(34) |
| <i>(E) C–C–C angles</i> | | | |
| C(16)–C(11)–C(12) | 118.47(45) | C(26)–C(21)–C(22) | 118.65(43) |
| C(11)–C(12)–C(13) | 121.29(51) | C(21)–C(22)–C(23) | 120.07(48) |
| C(12)–C(13)–C(14) | 119.66(56) | C(22)–C(23)–C(24) | 121.12(55) |
| C(13)–C(14)–C(15) | 120.51(56) | C(23)–C(24)–C(25) | 119.28(54) |
| C(14)–C(15)–C(16) | 120.14(53) | C(24)–C(25)–C(26) | 120.41(52) |
| C(15)–C(16)–C(11) | 119.91(48) | C(25)–C(26)–C(21) | 120.47(47) |
| C(36)–C(31)–C(32) | 119.30(47) | C(46)–C(41)–C(42) | 119.04(46) |
| C(31)–C(32)–C(33) | 120.28(50) | C(41)–C(42)–C(43) | 120.86(52) |
| C(32)–C(33)–C(34) | 119.93(59) | C(42)–C(43)–C(44) | 118.88(57) |
| C(33)–C(34)–C(35) | 121.00(66) | C(43)–C(44)–C(45) | 120.31(60) |
| C(34)–C(35)–C(36) | 120.18(64) | C(44)–C(45)–C(46) | 121.42(58) |
| C(35)–C(36)–C(31) | 119.28(54) | C(45)–C(46)–C(41) | 119.47(50) |
| C(56)–C(51)–C(52) | 118.71(44) | C(66)–C(61)–C(62) | 118.16(42) |
| C(51)–C(52)–C(53) | 120.82(48) | C(61)–C(62)–C(63) | 120.41(47) |
| C(52)–C(53)–C(54) | 119.86(54) | C(62)–C(63)–C(64) | 120.39(54) |
| C(53)–C(54)–C(55) | 119.96(56) | C(63)–C(64)–C(65) | 119.75(57) |
| C(54)–C(55)–C(56) | 120.89(54) | C(64)–C(65)–C(66) | 120.38(54) |
| C(55)–C(56)–C(51) | 119.72(48) | C(65)–C(66)–C(61) | 120.78(47) |
| <i>(F) Angles within the CF₃SO₃⁻ anion</i> | | | |
| O(4)–S–O(5) | 115.54(29) | S–C(5)–F(1) | 113.11(45) |
| O(4)–S–O(6) | 113.13(29) | S–C(5)–F(2) | 110.12(46) |
| O(5)–S–O(6) | 115.98(31) | S–C(5)–F(3) | 113.51(48) |
| C(5)–S–O(4) | 102.91(28) | F(1)–C(5)–F(2) | 104.23(54) |
| C(5)–S–O(5) | 103.96(30) | F(1)–C(5)–F(3) | 107.05(56) |
| C(5)–S–O(6) | 102.95(30) | F(2)–C(5)–F(3) | 108.30(57) |

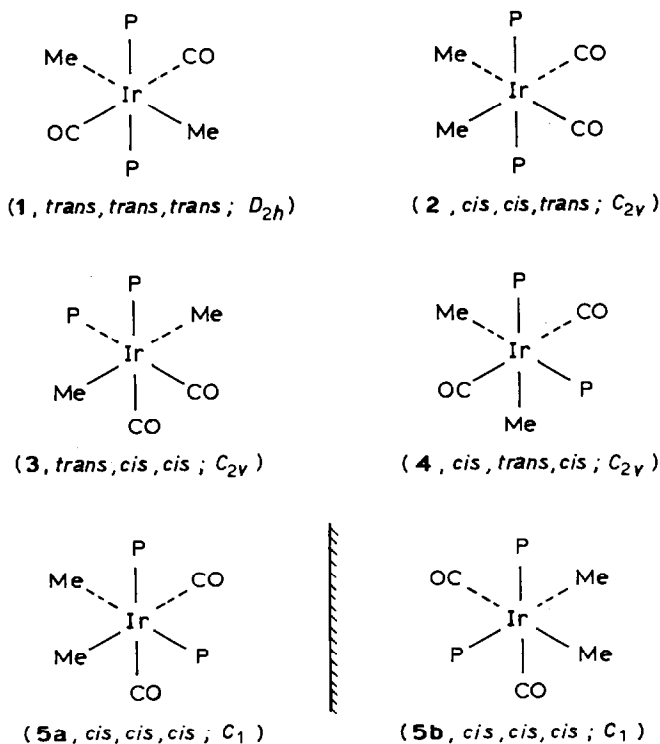


Fig. 4. Possible isomers of $[\text{Ir}(\text{CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]^+$ (designators refer, in turn, to the juxtaposition of methyl, carbonyl and triphenylphosphine (P) ligands and to the idealized local point group symmetry).

$[\text{CF}_3\text{SO}_3^-]$, does not result in the facile reductive elimination of C_2H_6 . Given the failure to cleanly form C_2H_6 from either $\text{Ir}(\text{CH}_3)_2(\text{I})(\text{CO})(\text{PPh}_3)_2$ or $[\text{Ir}(\text{CH}_3)_2(\text{CO})(\text{PPh}_3)_2]^+[\text{CF}_3\text{SO}_3^-]$ under moderate conditions, the existence of unusually strong transition metal–methyl bonds in these two complexes is implicated.

Additional material. A listing of observed and calculated structure factor amplitudes is available, upon request, from one of us (M.R.C.).

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