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Crystal Structure of the Quasitetrahedral Iridium(I) Complex, $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$. An Intermediate in Cyclotrimerization of Activated Alkynes by 16-Electron Alkyl Complexes of Iridium, *trans*-$RIr(CO)L_2$ ($R = Me, CH_2CMe_3$; $L = PPh_3, P(p\text{-tolyl})_3$)

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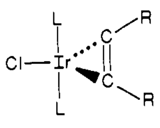
Abstract: Complexes *trans*-$RIr(CO)L_2$ ($R = Me, CH_2CMe_3$; $L = PPh_3$ or $P(p\text{-tolyl})_3$) are cyclotrimerization catalysts for activated acetylenes. Stoichiometric reaction between $C_2(CO_2Me)_2$ and *trans*-$Me_3CCH_2Ir(CO)[P(p\text{-tolyl})_3]_2$ results in the formation of $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$, an unusual tetrahedral, 16-electron, iridium(I) complex. An X-ray diffraction study confirms the geometry. The complex $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 11.125$ (2) Å, $b = 21.725$ (6) Å, $c = 20.889$ (5) Å, $\beta = 93.465$ (16)°, $V = 5039$ (2) Å^3, and $Z = 4$. Single-crystal X-ray diffraction data (Mo Kα, $2\theta = 5$–$45°$) were collected and the structure solved and refined to $R_F = 6.2\%$ for those 5196 data with $|F_o| > 3\sigma(|F_o|)$ [$R_F = 5.0\%$ for 4433 data with $|F_o| > 6\sigma(|F_o|)$]. If we regard the η^2-$C_2(CO_2Me)_2$ ligand as occupying a single stereochemical site (as is usually the case) the molecule is a tetrahedral complex of Ir(I) in which Ir–P = 2.334 (3) and 2.314 (3) Å, the Ir–C(acyl) bond length is 1.951 (13) Å, and Ir···cent (center of acetylenic linkage) = 1.941 Å. Interligand angles are P(1)–Ir–P(2) = 105.20 (10)°, P(1)–Ir–C(acyl) = 94.20 (36)°, P(1)–Ir–cent = 122.80°, P(2)–Ir–C(acyl) = 91.86 (36)°, P(2)–Ir–cent = 123.28°, and C(acyl)–Ir–cent = 111.15°. The mechanism of the cyclotrimerization reaction involves coordination of an acetylene molecule, an alkyl migration, coordination of a second acetylene molecule, metallacyclopentadiene formation, and cycloaddition of a third acetylene molecule leading to elimination of the derived benzenoid cyclotrimer.

Iridium(I) complexes have had a major impact on organometallic chemistry.[1-3] Vaska's compound and its analogues, i.e., *trans*-$Ir(CO)(PPh_3)_2X$ (X = Cl, Br, I, Me, OMe, etc.), and the related cations IrL_4^+ ($L_4 = (PMe_3)_4$ or $(dppe)_2$, etc.) have been examined extensively.[2,4-6] Many of these complexes have been characterized structurally and are invariably square planar as expected for four-coordinate derivatives of a d^8, third-row transition metal. In the course of our examination of the interaction of activated acetylenes with alkyl complexes of iridium,[7] $RIr(CO)L_2$ ($R = Me, CH_2CMe_3$; $L = PPh_3, P(p\text{-tolyl})_3$), we have characterized a complex that is not only an intermediate in the cyclotrimerization of acetylenes but also represents a unique example of a complex with a nearly tetrahedral arrangement of ligands around an iridium(I) center.

Interest in alkyne oligomerization has continued steadily since the discovery by Reppe of the tetramerization of acetylene to cyclooctatetraene.[8] The primary oligomerization products for acetylenes are polymers, cyclotetramers, and cyclotrimers (benzene derivatives).[9-11] Complexes of various metals are active as oligomerization catalysts for acetylenes. Some mechanistic research was carried out with iridium complexes.[12,13] *trans*-$Ir(N_2)(PPh_3)_2Cl$ is active as a catalyst at 110 °C for trimerization of activated acetylenes such as $MeO_2CC{\equiv}CCO_2Me$ (DMAD). Under moderate conditions the monoacetylene adduct (I) and diacetylene adduct (II) could be isolated.[12,13] Interestingly, the carbonyl analogue, *trans*-$Ir(CO)(PPh_3)_2Cl$, is inactive as a trimerization catalyst, although a monoacetylene adduct is formed.[12] Presumably the carbonyl ligand blocks the site necessary for coordination of a second acetylene moiety.



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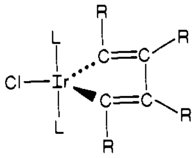

II

We have recently reported that *trans*-$MeIr(CO)(PPh_3)_2$ adds activated acetylenes to form both a kinetic and a thermodynamic isomer of $MeIr(CO)(PPh_3)_2$(acetylene).[7] In contrast to the chloro analogue, the methyl complex can open a coordination site by methyl migration. This allows a second acetylene molecule to coordinate and begin a catalytic cycle. In this paper we report the cyclotrimerization of activated acetylenes by *trans*-$RIr(CO)(PPh_3)_2$ ($R = Me, CH_2CMe_3$) under ambient conditions.

Experimental Section

All solvents were purified according to standard techniques and were then distilled from appropriate drying agents under a dry nitrogen atmosphere. All syntheses were accomplished under an argon atmosphere. Dimethylacetylenedicarboxylate (DMAD) and dimethoxybutyne (DMB) (Lancaster synthesis), and phenylacetylene, diphenylacetylene, 2-butyne, and methyl propargyl ether (Aldrich) were purified on neutral alumina and degassed prior to use. Iridium trichloride, $IrCl_3{\cdot}3H_2O$, was loaned by Johnson Matthey Inc. *trans*-$MeIr(CO)(PPh_3)_2$ and $MeIr(CO)$-

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(PPh$_3$)$_2$(DMAD) were prepared as previously described.[7] Infrared spectra were recorded on a Beckman 4240 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM390 or a Joelco FX90Q spectrometer. ^{13}C and ^{31}P NMR spectra were recorded on a Joelco FX90Q spectrometer.

IrCl(CO)[P(p-tolyl)$_3$]$_2$. In a typical reaction a flask was charged with 1.17 g of IrCl$_3$·3H$_2$O, 5.05 g of P(p-tolyl)$_3$, and 15 mL of DMF. The solution was refluxed for 11 h and then cooled to room temperature. The product was precipitated by the addition of 200 mL of 1:1 methanol–pentane. The fine yellow precipitate was collected by vacuum filtration. The product was purified by recrystallization from toluene/hexanes with a yield of 80%.

***trans*-Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]$_2$.** In a typical synthesis, 0.5 g of *trans*-IrCl(CO)[P(p-tolyl)$_3$]$_2$ was suspended in 10 mL of DME. To the suspension 2.5 equiv of Me$_3$CCH$_2$Li were added. The solution immediately became orange-red and was stirred for 60 min. Excess Me$_3$CCH$_2$Li was decomposed by addition of neutral alumina. The mixture was filtered through a fine sintered glass frit and the alumina washed with dimethoxyethane (DME) until the orange color was discharged. DME was removed under vacuum. The orange solid was extracted with cyclohexane and filtered. Removal of cyclohexane yielded an orange powder (yield 90%).

Reaction of *trans*-Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]$_2$ with $HC\equiv CCH_2OCH_3$. An NMR tube equipped with a 14/20 joint was charged with 12 mg (0.013 mmol) of *trans*-Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]^2. On a high-vacuum line, approximately 0.5 mL of C$_6$D$_6$ and 0.070 mmol of $HC\equiv CCH_2OCH_3$ were condensed into the tube at −196 °C. The tube was then flame sealed and warmed to room temperature. The reaction was monitored by ^{1}H NMR spectroscopy. The products neopentane and CH$_3$OCH$_2$C$\equiv$CIr(CO)[P(p-tolyl)$_3$]$_2$, were identified by ^{1}H NMR spectroscopy.

Preparation of Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$]. A flask was charged with 0.352 g (0.391 mmol) of Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]$_2$ and 14.50 mL of 0.0281 M DMAD in cyclohexane (0.407 mmol). After the mixture was stirred for 1.5 h, the volume of the solution was reduced to approximately 2 mL. The solution was transferred to a 1 × 15 cm alumina column where the product was eluted with 3:1 cyclohexane–THF as a yellow-orange solution. Removal of solvent provided a yellow-orange powder with an IR spectrum in KBr as follows: 1985, 1735, and 1652 cm^{-1}.

Preparation of Ir(COCH$_2$CMe$_3$)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$], Ir(CH$_2$CMe$_3$)(CO)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$] was dissolved in THF/methylcyclohexane and crystals were slowly deposited over a period of 4 days. The infrared spectrum between 2200 and 1600 cm^{-1} showed only an acyl stretch (1697 cm^{-1}) in addition to the DMAD stretches (1735 and 1652 cm^{-1}). The NMR spectra (^{1}H 3.42 (s), 3.20 (s), 2.08 (s), and 1.11 (s) ppm; ^{13}C 21.09 (q, J_{C-H} = 126.4 Hz), 29.59 (q, J_{C-H} = 124.5 Hz), 33.72 (s), 51.29 (q, J_{C-H} = 146.5 Hz), 70.7 ppm (t, J_{C-H} = 133.6 Hz; ^{31}P 8.70 (s) ppm) are consistent with the formulation.

Cyclotrimerization of C$_2$(CO$_2$Me)$_2$ by MeIr(CO)(PPh$_3$)$_2$. In an inert atmosphere glovebox a solution of 0.100 g of *trans*-MeIr(CO)(PPh$_3$)$_2$, 0.50 mL of DMAD, and 10 mL of benzene was prepared, placed in a reaction tube, and stirred at room temperature for 24 h. During this time the color of the solution changed from yellow to orange. The resulting solution was evaporated to dryness and the solid residue extracted in 15 mL of MeOH. Reduction of solution volume to 7 mL and cooling in an ice bath led to crystallization of a light orange solid which was collected and washed with small portions of cold MeOH to remove the orange impurity. The resulting solid was recrystallized from slowly evaporating MeOH to yield 0.23 g (40% based on C$_2$(CO$_2$Me)$_2$) of white crystalline product with a melting point (188–189 °C) and infrared (1735, 1225, and 1180 cm^{-1} in KBr) and ^{1}H NMR (3.85 (s) ppm in C$_6$D$_6$) spectra identical with those previously reported for C$_6$(CO$_2$Me)$_6$.[13]

The following procedure was used to quantitatively determine the cyclotrimerization of C$_2$(CO$_2$Me)$_2$ by ^{1}H NMR. In an inert atmosphere glovebox an NMR tube was loaded with 0.050 g of catalyst (*trans*-MeIr(CO)(PPh$_3$)$_2$ or the thermodynamic isomer of MeIr(CO)(PPh$_3$)$_2$[C$_2$(CO$_2$Me)$_2$]) and 0.25 mL of C$_6$D$_6$. The tube was then capped with a rubber septum, removed from the glovebox, and frozen at −78 °C. A solution (1 mL) containing 0.20 mL of C$_2$(CO$_2$Me)$_2$, 0.053 g of C$_6$Me$_6$, and C$_6$D$_6$ was injected and frozen and the NMR tube sealed. With use of a reference sample of C$_2$(CO$_2$Me)$_2$, C$_6$(CO$_2$Me)$_6$, and C$_6$Me$_6$ the spectrometer (EM 390) was tuned and set to "integration". The sample tube was then warmed and placed in the NMR and the spectrum integrated. Data collected in this manner indicated that C$_2$(CO$_2$Me)$_2$ is cyclotrimerized at 300 turnovers per hour. There appeared to be a short induction period for *trans*-MeIr(CO)(PPh$_3$)$_2$ in comparison to the thermodynamic isomer of MeIr(CO)(PPh$_3$)$_2$[C$_2$(CO$_2$Me)$_2$].

Table I. Experimental Data for the X-ray Diffraction Study of Ir(COCH$_2$CMe$_3$)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$]

(A) Unit Cell Data	
a = 11.125 (2) Å	crystal system: monoclinic
b = 21.725 (6) Å	space group: $P2_1/c$
c = 20.889 (5) Å	Z = 4
β = 93.465 (16)°	formula: C$_{54}$H$_{59}$IrP$_2$O$_5$
V = 5039 (2) Å^3	mol wt 1042.3
T = 24 °C (297 K)	D(calcd) = 1.37 g/cm^3
(B) Collection of X-ray Diffraction Data	
diffractometer:	Syntex P2$_1$
radiation:	Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710730 Å)
monochromator:	highly oriented (pyrolytic) graphite; equatorial mode with $2\theta(m)$ = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction
reflections measd:	$+h,+k,\pm l$ for $2\theta = 5 \rightarrow 45°$, yielding 6586 unique data
scan type:	coupled θ(crystal)–2θ(counter)
scan width:	$[2\theta(K\alpha_1) - 0.9]° \rightarrow [2\theta(K\alpha_2) + 0.9]°$
scan speed:	4.0 deg/min (2θ)
backgrounds:	stationary–crystal, stationary–counter at the two extremes of the 2θ scans; each for one–quarter of the total scan time
standard reflns:	three mutually orthogonal reflections collected before each set of 97 data points: no decay was observed
absorption correction:	μ(Mo Kα) = 29.2 cm^{-1}; corrected empirically by interpolation (in 2θ and ϕ) for 6 close–to–axial (ψ–scan) reflections

Reaction of MeIr(CO)(PPh$_3$)$_2$ with DMAD and DMB. An NMR tube was charged with 0.05 g of *trans*-MeIr(CO)(PPh$_3$)$_2$, 0.05 mL of DMAD, 0.05 mL of DMB and approximately 0.3 mL of C$_6$D$_6$. The reaction was monitored by ^{1}H NMR spectroscopy. The products are C$_6$(CO$_2$Me)$_6$, 62%, and o-C$_6$(CO$_2$Me)$_4$(CH$_2$OMe)$_2$, 38%.

Reaction of Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$] with DMAD. An NMR tube equipped with a 12/20 joint was charged with 0.050 g (0.048 mmol) of Me$_3$CCH$_2$Ir(CO)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$] on a high-vacuum line; 0.5 mL of C$_6$D$_6$ and 0.1 mL of DMAD were condensed into the tube at −196 °C. The tube was then flame sealed, warmed to room temperature, and monitored by ^{1}H NMR spectroscopy. The product, C$_6$(CO$_2$Me)$_6$, was identified by ^{1}H NMR.

Collection of X-ray Diffraction Data for Ir(COCH$_2$CMe$_3$)[P(p-tolyl)$_3$]$_2$[C$_2$(CO$_2$Me)$_2$]. A yellow crystal of approximate orthogonal dimensions 0.1 × 0.2 × 0.3 mm^3 was mounted along its extended axis in a thin-walled glass capillary, aligned and centered on a Syntex P2$_1$ automated four-circle diffractometer. Determination of the crystal's orientation matrix and unit cell parameters was carried out as described previously;[14] details appear in Table I. The observed diffraction symmetry (C_{2h}, $2/m$) and systematic absences ($h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$) indicated the centrosymmetric space group $P2_1/c$ (C_{2h}^5; No. 14).[15]

All data were corrected for absorption and for Lorentz and polarization factors. Data were placed on an approximately absolute scale by use of a Wilson plot.

Solution and Refinement of the Structure. All calculations were performed by use of a locally modified version of the Syntex XTL program package. The position of the iridium atom was determined from a Patterson map. All other non-hydrogen atoms were located from subsequent difference-Fourier maps. Parameters were refined with a least-squares procedure, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \{(\sigma(|F_o|))^2 + (0.015|F_o|)^2\}$. Refinement of positional and thermal values for all non-hydrogen atoms (anisotropic except for carbon atoms of the p-tolyl groups) led to convergence[16] with R_F = 6.2%, R_{wF} = 5.8%, and GOF = 1.84 for those 5196 data for which $|F_o| > 3\sigma(|F_o|)$ and R_F = 5.0% and R_{wF} = 5.5% for those 4433 data with $|F_o| > 6\sigma(|F_o|)$. Throughout the analysis, the calculated structure factors were based upon the analytical expression for neutral atoms' scattering factors; real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms.[17] The final difference-Fourier map showed no anomalous features, the strongest feature (of height 0.72 e$^-$/Å^3) being close to the position of the iridium atom. Final positional parameters appear in Table II.

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(16) $R_F(\%) = 100\sum||F_o| - |F_c||/\sum|F_o|$; $R_{wF}(\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO = number of observations and NV = number of variables.

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Table II. Final Positional and Isotropic Thermal Parameters for $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$

atom	*x*	*y*	*z*	*B*, Å^2
Ir	0.18860 (4)	−0.08286 (2)	0.28193 (2)	
P(1)	0.03796 (25)	−0.15522 (14)	0.29738 (13)	
P(2)	0.09280 (25)	−0.00290 (14)	0.22628 (13)	
O(1)	0.22168(78)	−0.09970 (44)	0.14894 (42)	
O(2)	0.4284(13)	−0.18498 (73)	0.38892 (80)	
O(3)	0.3561 (16)	−0.12343 (69)	0.45987 (60)	
O(4)	0.3968 (10)	0.05355 (55)	0.36658 (52)	
O(5)	0.51407 (76)	0.00257 (42)	0.30414 (48)	
C(1)	0.2374 (10)	−0.12055 (53)	0.20278 (64)	
C(2)	0.3050 (13)	−0.18419 (67)	0.20911 (71)	
C(3)	0.4265 (12)	−0.19005 (70)	0.17866 (69)	
C(4)	0.4716(19)	−0.25682 (86)	0.19924 (91)	
C(5)	0.5116(15)	−0.1453 (10)	0.2101 (10)	
C(6)	0.4143 (14)	−0.17999 (91)	0.10477 (75)	
C(1A)	0.3365 (10)	−0.04515 (62)	0.32940 (53)	
C(2A)	0.3150 (10)	−0.09695 (56)	0.35575 (57)	
C(3A)	0.3731 (15)	−0.13962 (85)	0.4054 (11)	
C(4A)	0.4342 (18)	−0.1730 (12)	0.50319 (85)	
C(5A)	0.4183 (12)	0.00944 (66)	0.33677 (66)	
C(6A)	0.5988 (13)	0.05565 (75)	0.30581 (85)	
C(11)	0.0867 (10)	−0.21954 (54)	0.35037 (55)	4.65 (26)
C(12)	0.0425 (14)	−0.22716 (77)	0.41057 (77)	8.52 (41)
C(13)	0.0830 (15)	−0.28221 (84)	0.44945 (79)	9.20 (45)
C(14)	0.1636 (13)	−0.31931 (70)	0.42653 (70)	7.00 (34)
C(15)	0.2057 (14)	−0.31530 (75)	0.36816 (77)	8.12 (39)
C(16)	0.1643 (13)	−0.26245 (74)	0.32881 (67)	7.60 (36)
C(17)	0.2071 (16)	−0.38055 (91)	0.46870 (85)	10.53 (50)
C(21)	−0.07814 (91)	−0.12004 (50)	0.34324 (49)	3.88 (22)
C(22)	−0.0387 (10)	−0.07929 (58)	0.39266 (52)	4.90 (24)
C(23)	−0.1248 (11)	−0.05113 (60)	0.43123 (58)	5.78 (29)
C(24)	−0.2459 (11)	−0.06467 (58)	0.42273 (59)	5.70 (29)
C(25)	−0.2863 (12)	−0.10459 (65)	0.37303 (66)	6.81 (34)
C(26)	−0.2012 (11)	−0.13181 (58)	0.33242 (57)	5.53 (28)
C(27)	−0.3378 (12)	−0.03476 (70)	0.46721 (67)	7.42 (36)
C(31)	−0.04595 (92)	−0.19707 (51)	0.23244 (50)	4.03 (23)
C(32)	−0.10758 (93)	−0.25022 (54)	0.24389 (50)	4.38 (23)
C(33)	−0.1736 (10)	−0.28237 (57)	0.19512 (56)	5.23 (28)
C(34)	−0.1793 (10)	−0.25669 (57)	0.13209 (54)	4.88 (25)
C(35)	−0.1165 (11)	−0.20343 (60)	0.11927 (58)	5.56 (28)
C(36)	−0.0455 (10)	−0.17250 (55)	0.16968 (53)	4.74 (26)
C(37)	−0.2561 (12)	−0.28772 (64)	0.07678 (63)	6.52 (32)
C(41)	0.18973 (94)	0.04992 (52)	0.18232 (49)	3.98 (22)
C(42)	0.1383 (11)	0.10162 (59)	0.15249 (59)	5.80 (30)
C(43)	0.2175 (13)	0.14575 (65)	0.12413 (63)	6.73 (33)
C(44)	0.3372 (13)	0.13673 (70)	0.12606 (66)	6.93 (34)
C(45)	0.3886 (12)	0.08219 (75)	0.15275 (65)	7.22 (33)
C(46)	0.3103 (12)	0.03858 (63)	0.18203 (62)	6.02 (30)
C(47)	0.4223 (15)	0.18428 (85)	0.09417 (79)	9.59 (46)
C(51)	0.03058 (91)	0.04991 (51)	0.28424 (19)	3.95 (22)
C(52)	0.0842 (10)	0.05309 (56)	0.34607 (57)	5.08 (27)
C(53)	0.0355 (11)	0.09433 (63)	0.39082 (60)	6.05 (30)
C(54)	−0.0668 (12)	0.12966 (67)	0.37433 (67)	6.82 (33)
C(55)	−0.1194 (12)	0.12865 (63)	0.31230 (64)	6.28 (31)
C(56)	−0.0682 (10)	0.08942 (61)	0.26652 (56)	5.63 (27)
C(57)	−0.1158 (14)	0.17405 (83)	0.42443 (77)	9.37 (44)
C(61)	−0.03323 (92)	−0.01767 (51)	0.16741 (50)	4.14 (23)
C(62)	−0.0141 (10)	−0.02350 (56)	0.10231 (56)	5.18 (27)
C(63)	−0.1130 (11)	−0.03741 (62)	0.05721 (59)	5.88 (29)
C(64)	−0.2263 (12)	−0.04423 (66)	0.08000 (66)	6.55 (32)
C(65)	−0.2480 (11)	−0.03925 (63)	0.14642 (62)	6.11 (30)
C(66)	−0.1492 (10)	−0.02728 (55)	0.19080 (55)	4.94 (26)
C(67)	−0.3376 (16)	−0.01767 (51)	0.03075 (83)	10.06 (48)

Results and Discussion

The complexes *trans*-$RIr(CO)L_2$ (R = Me, L = PPh_3; R = Me_3CCH_2, L = $P(p\text{-tolyl})_3$) readily add $C_2(CO_2Me)_2$. Other acetylenes such as C_2Ph_2, C_2Me_2, and $C_2(CH_2OMe)_2$ (DMB)

$$trans\text{-}RIr(CO)L_2 + [C_2(CO_2Me)_2] \rightarrow RIr(CO)L_2[C_2(CO_2Me)_2]$$

do not form complexes with the square-planar alkyl iridium complexes. Reaction of the alkyl complexes with terminal acetylenes leads, through oxidative addition of the C–H bond of the acetylene and reductive elimination of an alkyl C–H bond, to the alkane and the acetylide $RC{\equiv}CIr(CO)L_2$. When an excess of $C_2(CO_2Me)_2$ (DMAD) is used, cyclotrimerization of the acetylene occurs. The $C_6(CO_2Me)_6$ was recrystallized and carefully characterized.[13] For *trans*-$MeIr(CO)(PPh_3)_2$ the cyclotrimerization occurs at a rate of 300 turnovers/h at room temperature. The neopentyl complex, *trans*-$Me_3CCH_2Ir(CO)[P(p\text{-tolyl})_3]_2$, is much less active, with a cyclotrimerization rate of 3 turnovers/d.

The analogous halides are not active for DMAD trimerization, although an acetylene complex is formed.[12,13] It was suggested that the lack of an available coordination site prevented catalytic trimerization.[13] Evidently a path to cyclotrimerization exists for the alkyl complexes which does not exist for the halides. The most reasonable path to open a coordination site is an alkyl migration. We have previously suggested that alkyl-to-acyl steps are responsible for the catalytic activity of $MeCo(CO)_2[P(OMe)_3]_2$ in hydrogenation of alkenes.[19-21] Attempts to carbonylate $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$ led to replacement of $C_2(CO_2Me)_2$ by CO. We prepared the complex containing the larger neopentyl group in an attempt to force the alkyl migration.

The adduct of DMAD with *trans*-$Me_3CCH_2Ir(CO)[P(p\text{-tolyl})_3]_2$ undergoes a rearrangement to the four-coordinate CO

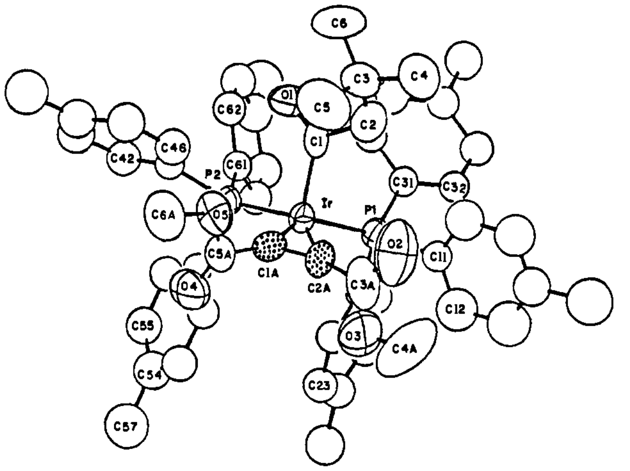

Figure 1. Labeling of non-hydrogen atoms in the $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ molecule (ORTEP-II diagram).

Table III. Selected Interatomic Distances (Å) for $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$

Ir–P(1)	2.334 (3)	Ir–C(1A)	2.040 (11)
Ir–P(2)	2.314 (3)	Ir–C(2A)	2.046 (12)
Ir–C(1)	1.951 (13)	Ir–cent[a]	1.941
C(1A)–C(2A)	1.282 (18)		

[a] Cent is the midpoint of the C(1A)–C(2A) bond.

Table IV. Selected Interatomic Angles (deg) for $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$

P(1)–Ir–P(2)	105.20 (10)	C(1)–Ir–C(1A)	108.85 (48)
P(1)–Ir–C(1)	94.20 (36)	C(1)–Ir–C(2A)	111.23 (48)
P(1)–Ir–C(1A)	140.15 (34)	C(1)–Ir–cent	111.15
P(1)–Ir–C(2A)	105.17 (34)	C(1A)–Ir–C(2A)	36.55 (47)
P(1)–Ir–cent	122.80		
P(2)–Ir–C(1)	91.86 (36)		
P(2)–Ir–C(1A)	106.02 (34)		
P(2)–Ir–C(2A)	139.96 (34)		
P(2)–Ir–cent	123.28		
Ir–C(1)–O(1)	126.60 (93)	Ir–C(1)–C(2)	116.92 (86)
Ir–C(1A)–C(2A)	71.98 (75)	Ir–C(2A)–C(1A)	71.47 (75)
Ir–C(1A)–C(5A)	146.65 (92)	Ir–C(2A)–C(3A)	149.0 (11)

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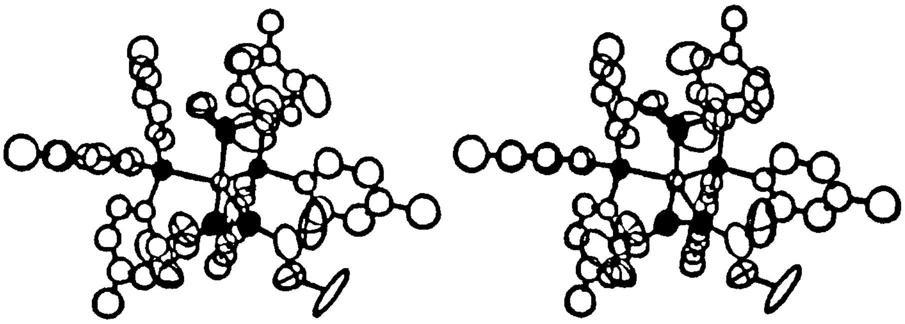

Figure 2. A stereoscopic view of the $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ molecule.

insertion product, $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$, which shows only an acyl stretch in the carbonyl region of the IR spectrum and an NMR spectrum consistent with the formulation.[22] To further characterize this unusual 16-electron acyl complex of Ir(I) we have determined its crystal structure.

Description of the Molecular Structure of $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$. The crystal contains an ordered arrangement of discrete molecular units of $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ that are separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. The overall geometry and labeling of the molecular core are shown in Figure 1. Figure 2 provides a stereoscopic view of the entire molecule. Interatomic distances and angles are listed in Tables III and IV, respectively.

The central iridium(I) atom has a coordination geometry perhaps best described as a distorted tetrahedron. The acyl group (based on C(1)) and two tri(p-tolyl)phosphine ligands occupy three sites with interligand angles of ∠P(1)–Ir–P(2) = 105.2 (1)°, ∠P(1)–Ir–C(1) = 94.2 (4)°, and ∠P(2)–Ir–C(1) = 91.9 (4)°. The acetylenic ligand is bound in its customary "side-on" (η^2) fashion. The acetylenic linkage (C(1A)–C(2A)) is approximately parallel to the P(1)···P(2) vector. The midpoint of the C(1A)–C(2A) bond, referred to as "cent", corresponds formally to the fourth tetrahedral site, with ∠cent–Ir–P(1) = 122.8°, ∠cent–Ir–P(2) = 123.4°, and ∠cent–Ir–C(1) = 111.2°. Angles to the atoms C(1A) and C(2A) include ∠P(1)–Ir–C(1A) = 140.2 (3)°, ∠P(2)–Ir–C(2A) = 140.0 (3)°, ∠P(1)–Ir–C(2A) = 105.2 (3)°, and ∠P(2)–Ir–C(1A) = 106.0 (3)°. The acetylene is bound symmetrically to iridium with essentially identical iridium–carbon distances, Ir–C(1A) = 2.040 (11) Å and Ir–C(2A) = 2.046 (12) Å. The iridium–cent distance is 1.941 Å and the acetylenic bond (C(2A)–C(1A)) is increased from approximately 1.20 Å in the free ligand to 1.282 (18) Å upon coordination to the iridium. The acetylene is apparently acting as a $2e^-$ donor and has the "cis-bent" configuration associated with angles at the acetylenic carbons of ∠C(5A)–C(1A)–C(2A) = 141.2 (12)° and ∠C(3A)–C(2A)–C(1A) = 138.8 (13)°. These values are in close agreement with those reported for the similar 18-electron Ir(I) complex, $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$[23] (viz., Ir–cent = 1.986 Å; C–C = 1.290 (23) Å, Ir–C(acetylene) = 2.113 (13) and 2.063 (14) Å; angles at the acetylenic carbons are 143 (2)° and 143 (2)°), and in the usual regime for mononuclear alkyne complexes.[24]

The iridium–phosphorus distances are Ir–P(1) = 2.334 (3) Å and Ir–P(2) = 2.314 (3) Å.

The iridium–acyl bond distance of 1.951 (13) Å is ~0.14 Å shorter than those reported for the octahedral Ir(III) complexes: $HIr[C(O)C_6H_3Et\text{-}6\text{-}CH_2\text{-}2][P(OMe)_3]_3$ and $HIr[C(O)C_6H_3Et\text{-}6\text{-}CH\text{-}CH_3\text{-}2][P(OMe)_3]_3$, 2.085 (12) Å and 2.097 (8) Å, respectively.[25]

The geometry and bond distances of the acetylene ligand suggest that it is acting as a $2e^-$ donor rather than as a $4e^-$ donor.[26-31] We were unable to observe the ^{13}C resonances for the alkyne carbons. If the DMAD were a $2e^-$ donor, the alkyne carbons could be obscured by the $P(p\text{-tolyl})_3$ resonances. Such was the case for DMAD as a $2e^-$ donor in $W(CO)_2(dppe)(DMAD)_2$.[31] We did not observe ^{13}C resonances in the 170-ppm region where the resonances from a $4e^-$ donor would be expected.[28] The complex, $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$, is thus an unsaturated, $16e^-$ Ir(I) complex which is potentially capable of undergoing oxidative addition and is of potential interest as a model for catalytic pathways.

The lack of paramagnetism in this d^8 complex suggests that the distortions from an ideal T_d geometry are sufficient to perturb the triple-degeneracy of the d_{xy}, d_{xz}, and d_{yz} orbitals. Although tetrahedral iridium complexes are not unknown, e.g., $[Ir(CO)_3(PPh_3)]^-$, they are rare and are typically $18e^-$, Ir(–I) complexes. The expected square-planar geometry does not occur in the present complex. Rearrangement from the electronically more favorable square-planar geometry to the sterically more favorable tetrahedral geometry is not unusual for *1st row* d^8 transition metals where Δ values are smaller.[32] Undoubtedly similar factors are operating here in that the tetrahedral arrangement minimizes steric interactions between the four bulky ligands. (A careful look at the stereoscopic Figure 2 shows that a site exists for a fifth ligand trans to the acyl ligand, but that access to this site is hindered by the two bulky tri(p-tolyl)phosphine ligands. It might be noted that if the fifth site were to be occupied with no other distortion occurring, the resulting stereochemistry about iridium would be trigonal bipyramidal with the η^2-acetylenic ligand in the expected orientation, parallel with the trigonal plane.)

The distortion from a regular tetrahedral coordination geometry which is observed for $Ir(COCH_2CMe_3)[Pt(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ is not toward a square-planar geometry but is a flattening of the regular tetrahedron to a trigonal pyramid as one might expect with steric interactions between three large groups pushing the three toward the smaller group. A distortion of T_d to C_{3v} does change the degeneracy of the d orbitals ($E + T_2 \rightarrow A_1 + 2E$).

There are two unique features of the compound $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$. The first, as discussed above, is that the complex is $16e^-$, four-coordinate Ir(I) complex that is tetrahedral rather than square planar. The second

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[22] The assignments are as follows for the ^{13}C NMR spectrum: 21.09, sp^3 carbon on tolyl ligand; 29.59, methyl carbon of neopentyl; 33.72, methyne carbon of neopentyl; 51.29, methyl carbon on DMAD; 70.70, methylene carbon of neopentyl; and 129–140, aromatic. And for the ^1H NMR spectrum: 1.11, methyl protons of neopentyl; 2.08, methyl protons of tolyl; 3.20, methylene protons of neopentyl; 3.42, methyl protons of DMAD; and 6.9–7.7, aromatic protons.

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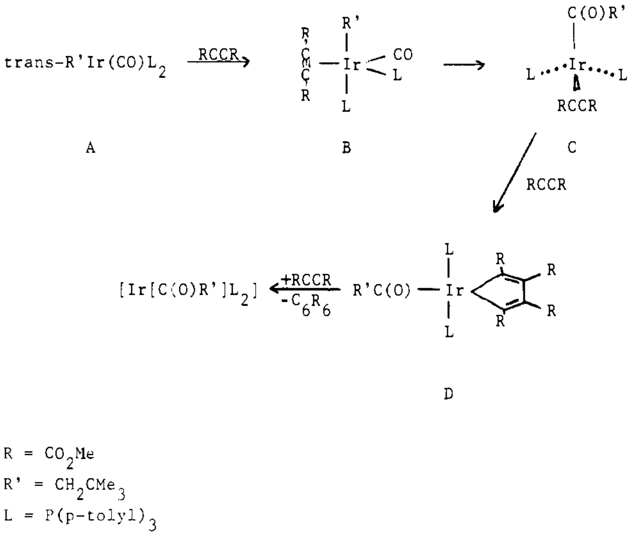

Figure 3. A scheme consistent with the experimental data for the cyclotrimerization of $C_2(CO_2Me)_2$. Structures have been determined for A, B, and C for these complexes and for D with the acyl replaced by Cl. The third acetylene is added in a Diels–Alder type reaction. Where the catalytic cycle is reentered depends on the relative rates of decarbonylation and acetylene association for the 14e$^-$ acyl.

is that the complex is a 16e$^-$ acyl complex which *does not* undergo alkyl migration to form the 18e$^-$ alkyl. Such a migration is observed in five-coordinate benzyl complexes[33] and must be involved in the rearrangement of $Ir(COMe)(CO)_2(PPh_3)_2$ to the 16e$^-$ alkyl complex *trans*-$MeIr(CO)(PPh_3)_2$.[34] Indeed, the analogous methyl complex of DMAD exists as the five-coordinate methyl complex, $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$. Each of these unique features of the neopentyl complex must be attributed to steric interactions. The larger neopentyl group forces the five-coordinate DMAD adduct to rearrange to the 16e$^-$ acyl, where steric interactions prevent a square-planar complex and force the tetrahedral arrangement.

Mechanism of Cyclotrimerization. The complexes *trans*-$MeIr(CO)(PPh_3)_2$ and $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$ are active for cyclotrimerization of DMAD at 300 turnovers/h under ambient conditions. Coordination of a second DMAD molecule probably occurs by a methyl migration leading to $Ir(COMe)(PPh_3)_2[C_2(CO_2Me)_2]_2$ which would rearrange to a metallacyclopentadiene complex.[13] This is supported by three pieces of evidence: (1) the identification of $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ for the neopentyl analogue; (2) the halide analogues, *trans*-$Ir(CO)(PPh_3)_2X$, are inactive for cyclotrimerization;[13] and (3) a metallacyclopentadiene complex was isolated for reaction of DMAD with *trans*-$Ir(N_2)(PPh_3)_2Cl$ since the N_2 ligand readily dissociates.[13] Once the metallacyclopentadiene complex is formed, the addition of the third acetylene molecule could occur by two possible suggested mechanisms. The first involves coordination of an acetylene, formation of metallacycloheptatriene, and then reductive elimination. The second involves a cycloaddition to form a bridged bicyclic complex in a Diels–Alder type reaction. To differentiate between these two steps we used a mixture of DMAD and DMB ($C_2(CH_2OMe)_2$), an acetylene which does not coordinate appreciably to these iridium complexes and is not itself cyclotrimerized. Use of a 1:1 ratio leads to $C_6(CO_2Me)_6$ (62%) and $C_6(CO_2Me)_4(CH_2OMe)_2$ (38%). The presence of *o*-$C_6(CO_2Me)_4(CH_2OMe)_2$ as a product suggests that the third acetylene molecule is added by the second mechanism, a cycloaddition. A scheme describing the mechanism is shown in Figure 3.

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Supplementary Material Available: Tables of anisotropic thermal parameters and bond distances and angles (5 pages); listing of observed and calculated structure factor amplitudes for $Ir(COCH_2CMe_3)[P(p\text{-tolyl})_3]_2[C_2(CO_2Me)_2]$ (31 pages). Ordering information is given on any current masthead page.

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Bromination of Bicyclobutanes: A Possible Case of an Electron-Transfer Mechanism[1]

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Abstract: The kinetics and product distribution of the bromination of 3-R-bicyclobutanecarbonitrile (R = H, Me, Cl, and Ph) by Br_2 and Br_3^- were studied in MeOH at 25 °C. For the first three substrates, the addition of Br–Br and Br–OMe across the central bond of the bicyclobutane moiety was (within experimental error) 100% syn stereospecific. For the phenylated substrate, where a relatively stable benzylic cation is formed, a mixture of syn and anti addition products was obtained. Reaction rate constants are best correlated by σ^+ with ρ^+ values of −6.2 and −6.4 for Br_2 and Br_3^-, respectively. In both cases the phenylated substrate deviates positively from the Hammett-type plot. With use of ab initio calculations it was shown that the mechanism that promotes the stereospecific syn additions in the acid-catalyzed additions to the same substrates is not operative in the case of the bromination reactions. Analogous to the electrophilic additions to aromatic and olefinic substrates, an electron-transfer mechanism is suggested for these reactions. Ab initio calculations (URHF) show that the bicyclobutane radical cation formed in the first step is more stable in the puckered form by ca. 18 kcal/mol as compared to the planar one.

Electrophilic attacks on bicyclobutane could in principle occur from the axial as well as the equatorial directions. However, a literature survey indicates that bicyclobutane undergoes electrophilic attacks exclusively from the equatorial direction.[3] The cause

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