

**ADDITION OF $C_2(CO_2Me)_2$ TO *trans*-MeIr(CO)(PPh₃)₂.
 FORMATION AND ISOMERIZATION OF MeIr(CO)(PPh₃)₂[C₂(CO₂Me)₂],
 AND CRYSTAL STRUCTURE OF THE THERMODYNAMIC ISOMER**

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(Received June 30th, 1986)

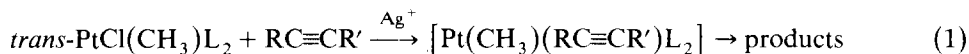
Summary

The reaction of $C_2(CO_2Me)_2$ with *trans*-MeIr(CO)(PPh₃)₂ leads to a kinetic isomer which has been characterized by ¹H and ³¹P NMR and infrared spectra and to a thermodynamic isomer which has been characterized by ¹H and ³¹P NMR, infrared, microanalysis and X-ray crystallography. The isomerization occurs readily in solution at room temperature; somewhat more slowly at –20°C. The thermodynamically stable isomer of MeIr(CO)(PPh₃)₂[C₂(CO₂Me)₂] crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a 14.847(2), b 16.648(2), c 15.656(3) Å, β 90.595(14)°, V 3869.7(11) Å³ and $Z = 4$. Single-crystal X-ray diffraction data were collected with a Syntex P2₁ automated diffractometer (Mo- K_α radiation, 2θ 5–40°) and the structure was solved and refined to R_F 8.6% for all 3631 independent data (R_F 4.0% for those 2318 data with $|F_o| > 6\sigma(|F_o|)$). The Ir^I center has a trigonal-bipyramidal environment with the methyl ligand and one PPh₃ ligand occupying axial sites (Ir–Me 2.193(14), Ir–P(1) 2.425(4) Å). The C₂(CO₂Me)₂ ligand is π -bonded to the iridium atom and lies with its triple bond parallel to the equatorial coordination plane; the equatorial ligands are completed by the second PPh₃ ligand (Ir–P(2) 2.402(3) Å) and a CO ligand (Ir–CO 1.812(15) Å).

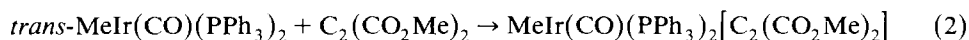
Acetylene complexes are important in many oligomerization and polymerization reactions [1]. A step of potential importance is the insertion of an alkyne into a metal carbon sigma bond. Our recent synthesis of *trans*-MeIr(CO)(PPh₃)₂ allows possible modeling of this step by reaction with alkynes [2].

* Alfred P. Sloan Foundation Fellow.

Transition metal alkyne chemistry has been investigated a number of years and reviewed extensively [1,3–6]. These reviews have centered on the preparations, reactions and structures of alkyne complexes. The majority of acetylene complexes involve metal–metal bonded systems or nickel group (Group 10) metals. Reaction of acetylene complexes are often quite complicated with the specific reactions observed depending on subtle factors. Addition of acetylene to “PtL₂CH₃⁺” was shown to give different products (see eq. 1) depending on the nature of the acetylene, the ligands L, the solvent and the reaction conditions [7–10].



Our high-yield synthesis of the sixteen-electron methyl complex, *trans*-MeIr(CO)(PPh₃)₂ which readily adds acetylene molecules, allows further study of the possible interaction of a methyl group with coordinated acetylene [2]. In this paper we report the reaction of *trans*-MeIr(CO)(PPh₃)₂ with C₂(CO₂Me)₂ (eq. 2),



which leads to a kinetic isomer and a thermodynamic isomer. Both isomers have been characterized and their structures assigned.

Experimental

Iridium trichloride was generously loaned by Johnson Matthey Inc. All solvents were dried and degassed prior to use. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer and ¹H NMR spectra were recorded on a Varian EM 390 or on a JEOL FX 90Q. *Trans*-Ir(PPh₃)₂(CO)Cl and *trans*-MeIr(CO)(PPh₃)₂ were prepared as previously described [2,11].

Synthesis of the kinetic isomer of MeIr(CO)(PPh₃)₂[C₂(CO₂Me)₂]

In an inert atmosphere glove box 0.20 g of *trans*-MeIr(CO)(PPh₃)₂ were placed in a Schlenk flask, sealed, brought out of the box, flushed with N₂ and immersed in a –20°C bath. The acetylene (4.0 ml of a 7 × 10^{–2} M solution in benzene) was added to the chilled flask while flushing with N₂. The resulting pale yellow suspension was stirred for 15 min at –20°C and pentane (20 ml) slowly added. The resulting mixture was stirred for an additional 5 min. The pale yellow solid was collected by suction filtration and washed (3 × 5 ml) with pentane. The yield was 0.16 g (67%). The infrared spectrum in KBr is: 1945vs (assigned to C≡O stretch), 1750m-br (assigned to C≡C stretch) and 1680s cm^{–1} (assigned to C=O stretch) and the ¹H NMR (–20°C) spectrum is: 6.99(m) (assigned to PPh₃), 3.22(s) and 3.04(s) (assigned to OCH₃'s) and 1.25(t) ppm *J*(P–H) 5.3 Hz (assigned to Ir–CH₃). The ³¹P NMR (proton decoupled) at –20°C in toluene-*d*₈ shows a singlet at 7.67 ppm (reference H₃PO₄).

Synthesis of the thermodynamic isomer of MeIr(CO)(PPh₃)₂[C₂(CO₂Me)₂]

In an inert atmosphere glove box 0.20 g *trans*-MeIr(CO)(PPh₃)₂ and 4.0 ml of a 7 × 10^{–2} M benzene solution of C₂(CO₂Me)₂ (1.08 equiv.) were allowed to stir for 4 h at room temperature. The solution was evaporated to dryness and the resulting solid chromatographed on an alumina column (1/1 benzene/THF). The first band

(golden-yellow) was collected and evaporated to dryness to yield 0.17 g (72%) of air-stable yellow powder. Diffraction grade crystals may be prepared by slowly chilling (first to 0°C, then to -20°C) a saturated solution of MeIr(CO)(PPh₃)₂[C₂(CO₂Me)₂] in toluene/hexane (70/30) for 24 h. Microanalysis: Found: C, 58.48; H, 4.37; P, 6.94. calc: C, 58.59; H, 4.33; P, 6.88%. Infrared (KBr): 1975vs (C=O), 1781m-br (C≡C), 1688s and 1678s cm⁻¹ (C=O). ¹H NMR (20°C): 7.0(m) (PPh₃) 3.46(s) and 3.31(s) (O-CH₃'s) and 0.60 ppm (dd) *J*(P-H) 5.9 and *J*(P-H) 7.9 Hz. ³¹P NMR (-20°C): 0.24(d), *J*(P-P) 8.3 Hz and -6.04(d) ppm, *J*(P-P) 8.3 Hz.

Collection of diffraction data

The crystal chosen for the X-ray structural analysis was a yellow transparent parallelepiped having approximate orthogonal dimensions of 0.1 × 0.2 × 0.2 mm³. The crystal was sealed into a thin-walled glass capillary under an inert atmosphere (Ar) since it seemed probable that it might be sensitive to air or moisture. The crystal was aligned accurately on a Syntex P2₁ automated four-circle diffractometer. Subsequent set-up operations and collection of the X-ray diffraction data were carried out as described previously [13]; details appear in Table 1. The observed diffraction symmetry (*C*_{2h}, 2/*m*) and the systematic absences (*h*0*l* for *l* = 2*n* + 1; 0*k*0 for *k* = 2*n* + 1) indicated that the crystal belonged to the centrosymmetric monoclinic space group *P*2₁/*c* (*C*_{2h}⁵; No. 14).

All data were corrected for the effects of absorption and for Lorentz and polarization factors and were converted to unscaled |*F*_o| values. Any reflection

(Continued on p. 416)

TABLE 1

CRYSTALLOGRAPHIC DATA FOR MeIr(CO)(PPh₃)₂[C₂(CO₂Me)₂]

Crystal parameters at 24°C (297 K)

Crystal system: monoclinic	Formula: C ₄₄ H ₃₉ IrO ₅ P ₂
Space group: <i>P</i> 2 ₁ / <i>c</i> (No. 14)	Molec. wt.: 901.95
<i>a</i> 14.847(2) Å	<i>Z</i> = 4
<i>b</i> 16.648(2) Å	<i>D</i> (calc) 1.55 g cm ⁻³
<i>c</i> 15.656(3) Å	<i>μ</i> (Mo- <i>K</i> _α) 37.9 cm ⁻¹
<i>β</i> 90.595(14)°	
<i>V</i> 3869.7(11) Å ³	

Collection of X-ray diffraction data

Diffractometer: Syntex P2₁
 Radiation: Mo-*K*_α (λ 0.710730 Å)
 Monochromator: Highly oriented (pyrolytic) graphite, 2*θ*(m) 12.160° for 002 reflection; equatorial mode; assumed 50% perfect/50% ideally mosaic for polarization correction
 Reflections measured: + *h*, + *k*, ± *l* for 2*θ* = 5.0–40.0°; 4119 reflections merged to 3631 unique data
 Scan-type: coupled *θ*(crystal)–2*θ*(counter)
 Scan-speed: 2.50°/min
 Scan width: [2*θ*(*K*_{α1}) – 1.0] – [2*θ*(*K*_{α2}) + 1.0]°
 Backgrounds: stationary-crystal and stationary-counter; measured at each end of the 2*θ* scan (each for one-half total scan time)
 Standards: 3 remeasured after each batch of 97 reflections; no significant fluctuations observed

TABLE 2

FINAL POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS FOR $\text{MeIr}(\text{CO})\text{-}(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$

Atom	x	y	z	B_{iso}
Ir	0.26384(4)	0.04994(3)	0.22997(3)	
P(1)	0.15749(25)	0.01517(21)	0.34051(21)	
P(2)	0.25092(23)	-0.06535(21)	0.13839(21)	
C(1)	0.1828(11)	0.11370(90)	0.17548(92)	
O(1)	0.13380(75)	0.16003(67)	0.13991(69)	
C(2)	0.3690(10)	0.09618(90)	0.14578(86)	
C(3)	0.5049(13)	-0.1035(11)	0.4471(11)	
O(3)	0.42850(71)	-0.05226(72)	0.41526(65)	
C(4)	0.4489(12)	0.0020(11)	0.3552(10)	
O(4)	0.52526(81)	0.01202(68)	0.33049(70)	
C(5)	0.37028(92)	0.0477(11)	0.32054(80)	
C(6)	0.3337(10)	0.11793(91)	0.31860(85)	
C(7)	0.3441(10)	0.2002(10)	0.3501(10)	
O(7)	0.30991(81)	0.25729(64)	0.31654(70)	
O(8)	0.39904(68)	0.20257(59)	0.41722(67)	
C(8)	0.4110(13)	0.28260(95)	0.4549(10)	
C(11)	0.04200(76)	0.04504(79)	0.31873(72)	3.05(25)
C(12)	0.00299(94)	0.03166(80)	0.23836(84)	4.20(32)
C(13)	-0.0839(10)	0.0553(10)	0.21875(87)	5.19(34)
C(14)	-0.1359(10)	0.09349(91)	0.2784(10)	5.26(37)
C(15)	-0.1004(10)	0.10635(89)	0.3564(10)	5.06(36)
C(16)	-0.0134(10)	0.08186(84)	0.37948(88)	4.69(35)
C(21)	0.18524(80)	0.06699(76)	0.43975(76)	3.29(28)
C(22)	0.17496(91)	0.14987(84)	0.44485(86)	4.12(32)
C(23)	0.1963(10)	0.19060(92)	0.5196(10)	5.32(37)
C(24)	0.2276(11)	0.1523(11)	0.5888(11)	6.59(42)
C(25)	0.2392(12)	0.0705(12)	0.5871(11)	7.76(48)
C(26)	0.2180(10)	0.02823(90)	0.5108(10)	5.61(39)
C(31)	0.14786(85)	-0.08965(72)	0.37357(74)	2.72(27)
C(32)	0.0684(10)	-0.12492(86)	0.39341(85)	4.34(33)
C(33)	0.0668(11)	-0.2060(10)	0.4167(10)	5.74(39)
C(34)	0.1426(11)	-0.2503(10)	0.4175(10)	5.71(39)
C(35)	0.2252(11)	-0.21691(94)	0.39667(94)	5.41(37)
C(36)	0.22570(94)	-0.13414(85)	0.37506(85)	4.14(32)
C(41)	0.28552(78)	-0.04494(82)	0.02761(72)	3.18(26)
C(42)	0.3466(10)	-0.09393(86)	-0.01117(91)	4.57(34)
C(43)	0.3747(11)	-0.0752(10)	-0.0968(10)	5.90(41)
C(44)	0.3377(11)	-0.01267(95)	-0.1374(10)	5.31(37)
C(45)	0.2795(10)	-0.03793(92)	-0.10047(91)	5.12(35)
C(46)	0.25350(92)	0.02019(81)	-0.01739(89)	4.34(33)
C(51)	0.31823(84)	-0.15513(76)	0.16791(75)	3.02(28)
C(52)	0.2946(10)	-0.23144(88)	0.13668(86)	4.47(33)
C(53)	0.3501(11)	-0.29562(93)	0.1578(10)	5.55(38)
C(54)	0.4230(12)	-0.2847(11)	0.2065(10)	6.56(42)
C(55)	0.4525(11)	-0.2119(11)	0.2339(10)	6.73(43)
C(56)	0.3969(10)	-0.14513(94)	0.21051(93)	5.30(37)
C(61)	0.13773(85)	-0.10780(75)	0.12284(79)	3.07(29)
C(62)	0.08145(91)	-0.08381(77)	0.05491(81)	3.79(31)
C(63)	-0.0070(10)	-0.11197(88)	0.05003(92)	4.80(36)
C(64)	-0.0390(10)	-0.16100(91)	0.11053(93)	4.82(35)
C(65)	0.0132(10)	-0.18872(85)	0.17535(91)	4.76(34)
C(66)	0.10273(90)	-0.16116(81)	0.18176(81)	3.81(30)

TABLE 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
H(12)	0.0374	0.0054	0.1958	6.0
H(13)	-0.1080	0.0451	0.1633	6.0
H(14)	-0.1954	0.1103	0.2648	6.0
H(15)	-0.1358	0.1332	0.3976	6.0
H(16)	0.0081	0.0901	0.4361	6.0
H(22)	0.1531	0.1788	0.3966	6.0
H(23)	0.1884	0.2471	0.5217	6.0
H(24)	0.2418	0.1817	0.6392	6.0
H(25)	0.2610	0.0427	0.6360	6.0
H(26)	0.2267	-0.0282	0.5089	6.0
H(32)	0.0142	-0.0947	0.3914	6.0
H(33)	0.0114	-0.2301	0.4322	6.0
H(34)	0.1395	-0.3055	0.4326	6.0
H(35)	0.2789	-0.2479	0.3968	6.0
H(36)	0.2811	-0.1089	0.3613	6.0
H(42)	0.3702	-0.1395	0.0178	6.0
H(43)	0.4189	-0.1071	-0.1241	6.0
H(44)	0.3533	-0.0035	-0.1952	6.0
H(45)	0.2570	0.0838	-0.1297	6.0
H(46)	0.2115	0.0547	0.0095	6.0
H(52)	0.2422	-0.2388	0.1021	6.0
H(53)	0.3358	-0.3478	0.1372	6.0
H(54)	0.4565	-0.3307	0.2231	6.0
H(55)	0.5063	-0.2056	0.2664	6.0
H(56)	0.4157	-0.0923	0.2253	6.0
H(62)	0.1035	-0.0485	0.0123	6.0
H(63)	-0.0448	-0.0962	0.0036	6.0
H(64)	-0.1004	-0.1768	0.1077	6.0
H(65)	-0.0099	-0.2258	0.2156	6.0
H(66)	0.1399	-0.1795	0.2274	6.0

Atom	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Ir	3.215(26)	2.384(24)	2.402(24)	-0.216(30)	0.092(17)	0.053(27)
P(1)	3.48(19)	2.89(18)	2.48(16)	0.17(15)	0.26(15)	0.04(14)
P(2)	3.21(18)	3.00(20)	2.93(17)	0.13(15)	0.09(14)	-0.28(15)
C(1)	5.3(10)	3.63(88)	3.79(84)	-0.61(73)	0.23(71)	-0.22(65)
O(1)	6.65(73)	5.40(68)	6.46(68)	0.26(57)	-0.32(56)	1.92(54)
C(2)	5.20(88)	6.02(90)	3.90(77)	-2.01(73)	1.36(67)	0.61(67)
C(3)	8.9(12)	7.4(11)	9.0(12)	3.3(10)	-5.8(10)	2.60(91)
O(3)	7.33(68)	6.17(62)	5.09(57)	-1.00(66)	-1.09(52)	0.70(60)
C(4)	3.75(94)	6.9(11)	3.48(85)	-1.19(91)	-0.23(79)	-2.18(78)
O(4)	5.22(67)	7.87(76)	6.77(68)	1.36(58)	-0.58(58)	0.89(55)
C(5)	3.41(80)	5.20(94)	3.78(72)	-1.41(83)	-0.53(60)	-0.09(77)
C(6)	4.62(87)	2.83(81)	3.75(79)	-0.58(71)	1.03(63)	-0.61(64)
C(7)	3.22(81)	4.2(10)	4.65(92)	0.53(72)	0.26(72)	-0.84(77)
O(7)	9.93(85)	2.92(57)	7.57(72)	0.98(57)	-3.13(63)	0.05(50)
O(8)	5.11(60)	5.21(63)	6.11(61)	0.09(48)	-2.08(53)	-1.03(50)
C(8)	11.0(14)	4.38(93)	7.6(11)	-1.41(91)	-1.7(10)	-4.11(82)

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

with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. Data were placed on an approximately absolute scale by means of a Wilson plot.

Solution and refinement of the structure of $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$

All calculations were performed on our locally-modified version of the Syntex XTL interactive crystallographic program package [14]. Throughout the analysis the calculated structure factors were based upon the analytical expression for the neutral atoms' scattering factors; both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms [15].

The position of the iridium atom was quickly and unambiguously determined from a Patterson map. All remaining non-hydrogen atoms were located from a subsequent difference-Fourier map. The structure was refined by a least-squares refinement procedure, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $1/w = \{[\sigma(|F_o|)]^2 + [0.015|F_o|]^2\}$. All phenyl hydrogens were included in their idealized positions based upon $d(\text{C-H})$ 0.95 Å [16] and trigonal planar geometry about carbon. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms led to final convergence [17] with R_F 8.6, R_{wF} 5.0% and $GOF = 1.24$ for 289 parameters refined against all 3631 independent data. [Residuals for those 2774 data with $|F_o| > 3\sigma(|F_o|)$ were R_F 5.4 and R_{wF} 4.5%; for those 2318 data with $|F_o| > 6\sigma(|F_o|)$, R_F 4.0 and R_{wF} 3.9%.] As can be seen from these statistics, the diffraction data were rather weak, with only 63.8% being above $6\sigma(|F_o|)$ (i.e., $3\sigma(I)$) in intensity. Data collection was terminated at $2\theta = 40^\circ$ for this reason.

A final difference-Fourier map revealed possible positions for two of the three hydrogen atoms of the methyl ligand; this aspect was not further pursued. No other significant peaks were discernible. The structure is thus correct. Final positional parameters and anisotropic thermal parameters appear in Table 2.

A minor correction for the effects of secondary extinction was included using eq. 3; the value determined for g was 9.64×10^{-8} .

$$|F_{o,\text{corr}}| = |F_{o,\text{uncorr}}| (1.0 + gI_o) \quad (3)$$

Results and discussion

The acetylene complex, $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$, is readily formed by addition of the acetylene to the sixteen-electron methyl complex (eq. 2). The initial kinetic product which can be isolated at -20°C , slowly isomerizes to the thermodynamic product at room temperature. The isomerization can be followed by infrared spectral changes or by ^1H and ^{31}P NMR. The kinetic isomer shows equivalent triphenylphosphines (CH_3 is a triplet in ^1H NMR and a singlet in the ^{31}P NMR), while the thermodynamic isomer has inequivalent triphenylphosphines (CH_3 is a doublet of doublets and two doublets are observed in the ^{31}P NMR). To better define the isomerization reaction and the structures of the kinetic and thermodynamic products, the structure of the thermodynamic product was determined.

Description of the molecular structure of $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$

The scheme used for labelling this molecule is shown in Fig. 1. Interatomic distances and angles are listed in Tables 3 and 4, while a stereoscopic view of the molecule is provided by Fig. 2.

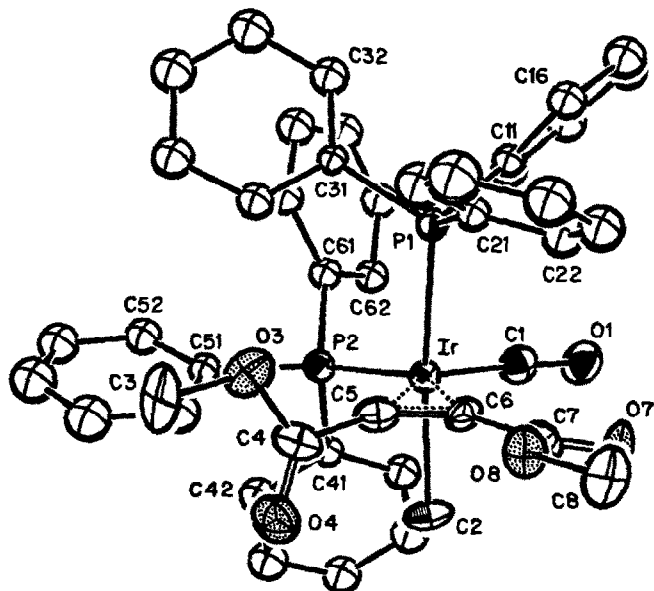


Fig. 1. Labelling of atoms within the $\text{MeIr(CO)(PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$ molecule. [ORTEP-II diagram, with all hydrogen atoms deleted.]

The central iridium(I) atom has a coordination environment somewhat distorted from an idealized trigonal bipyramidal geometry. The methyl group (defined by C(2)) and a triphenylphosphine ligand occupy the axial sites, with P(1)-Ir-C(2) $170.3(4)^\circ$. The remaining triphenylphosphine ligand (bonded through atom P(2)) a carbonyl ligand (linked via C(1)) and the $\text{C}_2(\text{CO}_2\text{Me})_2$ ligand (linked to iridium from "Cent", the mid-point of the C(5)-C(6) triple bond) complete the set of

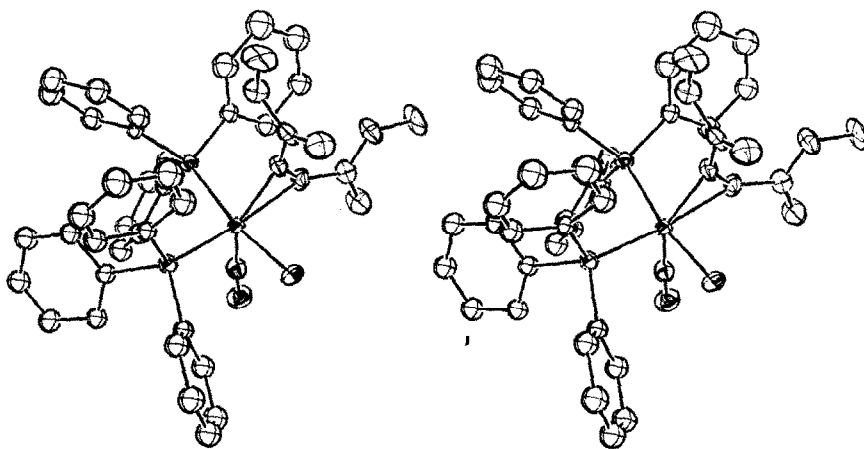


Fig. 2. Stereoscopic view of the $\text{MeIr(CO)(PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$ molecule.

TABLE 3
 INTERATOMIC DISTANCES (Å) FOR $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$

<i>(A) Iridium–ligand distances</i>			
Ir–P(1)	2.425(4)	Ir–C(2)	2.193(14)
Ir–P(2)	2.402(3)	Ir–C(5)	2.113(13)
Ir–C(1)	1.812(15)	Ir–C(6)	2.063(14)
C(1)–O(1)	1.194(19)	Ir–Cent ^a	1.986
<i>(B) Phosphorus–carbon distances</i>			
P(1)–C(11)	1.814(12)	P(2)–C(41)	1.846(12)
P(1)–C(21)	1.821(13)	P(2)–C(51)	1.854(13)
P(1)–C(31)	1.826(12)	P(2)–C(61)	1.837(13)
P–C(av.)	1.833 ± 0.015		
<i>(C) Distances within C₂(CO₂Me)₂ ligand</i>			
C(3)–O(3)	1.501(21)	C(8)–O(8)	1.467(19)
C(4)–O(3)	1.341(20)	C(7)–O(8)	1.324(19)
C(4)–O(4)	1.213(21)	C(7)–O(7)	1.196(19)
C(4)–C(5)	1.490(23)	C(6)–C(7)	1.464(22)
C(5)–C(6)	1.290(23)		
<i>(D) C–C distances in PPh₃ ligands</i>			
C(11)–C(12)	1.397(17)	C(14)–C(15)	1.341(21)
C(12)–C(13)	1.380(20)	C(15)–C(16)	1.398(21)
C(13)–C(14)	1.374(21)	C(16)–C(11)	1.405(18)
C(21)–C(22)	1.391(19)	C(24)–C(25)	1.373(26)
C(22)–C(23)	1.387(20)	C(25)–C(26)	1.419(24)
C(23)–C(24)	1.336(23)	C(26)–C(21)	1.371(20)
C(31)–C(32)	1.356(19)	C(34)–C(35)	1.389(23)
C(32)–C(33)	1.399(22)	C(35)–C(36)	1.419(21)
C(33)–C(34)	1.345(23)	C(36)–C(31)	1.373(19)
C(41)–C(42)	1.367(19)	C(44)–C(45)	1.342(21)
C(42)–C(43)	1.442(21)	C(45)–C(46)	1.392(20)
C(43)–C(44)	1.335(22)	C(46)–C(41)	1.375(19)
C(51)–C(52)	1.404(19)	C(54)–C(55)	1.356(25)
C(52)–C(53)	1.387(21)	C(55)–C(56)	1.430(23)
C(53)–C(54)	1.331(23)	C(56)–C(51)	1.349(20)
C(61)–C(62)	1.404(18)	C(64)–C(65)	1.352(20)
C(62)–C(63)	1.397(20)	C(65)–C(66)	1.409(20)
C(63)–C(64)	1.341(21)	C(66)–C(61)	1.386(18)
C–C(av.)	1.379 ± 0.029		

^a “Cent” is the midpoint of the triple bond C(5)–C(6).

equatorial ligands; angles of interest within the trigonal plane are P(2)–Ir–C(1) 98.0(5), P(2)–Ir–Cent 133.6 and C(1)–Ir–Cent 127.0°.

The axial and equatorial iridium–phosphorus distances are close to equivalent, with Ir–P(1) 2.425(4) and Ir–P(2) 2.402(3) Å. (A similar equivalence was found for $(\text{C}_7\text{H}_8)(\text{PMe}_2\text{Ph})_2\text{Ir}(\text{SnCl}_3)$ [18], but is neither expected nor required.) The equatorial alkyne ligand takes up the “parallel” conformation, with the initial triple bond, C(5)–C(6), lying in the equatorial trigonal coordination plane. This ligand appears to be slightly asymmetrically bound, with the Ir–C(5) distance of 2.113(13) Å being ~ 0.05 Å (close to 3σ) longer than the Ir–C(6) distance of 2.063(14) Å. This could be due to (i) the stronger *trans* influence of the carbonyl ligand acting on C(5) versus the PPh_3 ligand (through P(2)) acting on C(6) and/or (ii) the greater

TABLE 4
 INTERATOMIC ANGLES (°) FOR $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$

(A) Angles about the iridium atom

P(1)–Ir–P(2)	100.76(12)	C(1)–Ir–C(2)	89.1(6)
P(1)–Ir–C(1)	92.4(5)	C(1)–Ir–Cent ^a	127.0
P(1)–Ir–C(2)	170.3(4)	C(2)–Ir–Cent ^a	81.9
P(1)–Ir–Cent ^a	89.5	P(1)–Ir–C(5)	90.3(4)
P(2)–Ir–C(1)	98.0(5)	P(1)–Ir–C(6)	88.7(4)
P(2)–Ir–C(2)	88.6(4)	C(2)–Ir–C(5)	83.0(6)
P(2)–Ir–Cent ^a	133.6	C(2)–Ir–C(6)	81.7(6)
		C(5)–Ir–C(6)	36.0(6)

(B) Ir–P–C and C–P–C angles

Ir–P(1)–C(11)	114.9(4)	Ir–P(2)–C(41)	113.1(4)
Ir–P(1)–C(21)	110.7(4)	Ir–P(2)–C(51)	117.1(4)
Ir–P(1)–C(31)	118.9(4)	Ir–P(2)–C(61)	117.0(4)
C(11)–P(1)–C(21)	103.6(6)	C(41)–P(2)–C(51)	103.2(6)
C(11)–P(1)–C(31)	103.8(6)	C(41)–P(2)–C(61)	102.1(6)
C(21)–C(1)–C(31)	103.2(6)	C(51)–P(2)–C(61)	102.3(6)

(C) Ir–C–O angle

Ir–C(1)–O(1)	175.3(13)
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(D) Angles within $\text{C}_2(\text{CO}_2\text{Me})_2$ ligand

C(3)–O(3)–C(4)	116.1(13)	O(4)–C(4)–C(5)	123.0(15)
O(3)–C(4)–O(4)	122.3(15)	C(6)–C(7)–O(7)	123.5(14)
O(3)–C(4)–C(5)	114.6(14)	C(6)–C(7)–O(8)	110.9(13)
O(7)–C(7)–O(8)	125.5(14)	C(4)–C(5)–C(6)	143.0(15)
C(7)–O(8)–C(8)	114.6(12)	C(5)–C(6)–C(7)	143.0(15)
Ir–C(5)–C(4)	146.2(11)	Ir–C(6)–C(5)	74.1(9)
Ir–C(5)–C(6)	69.9(9)	Ir–C(6)–C(7)	142.3(11)

(E) C–C–P angles

C(12)–C(11)–P(1)	120.5(9)	C(42)–C(41)–P(2)	120.0(10)
C(16)–C(11)–P(1)	123.5(10)	C(46)–C(41)–P(2)	121.9(10)
C(22)–C(21)–P(1)	119.7(10)	C(52)–C(51)–P(2)	120.7(10)
C(26)–C(21)–P(1)	123.0(10)	C(56)–C(51)–P(2)	119.0(10)
C(22)–C(31)–P(1)	123.3(10)	C(62)–C(61)–P(2)	121.8(10)
C(26)–C(31)–P(1)	116.9(10)	C(66)–C(61)–P(2)	120.5(10)

(F) C–C–C angles within PPh_3 ligands

C(12)–C(11)–C(16)	116.0(12)	C(22)–C(21)–C(26)	117.3(12)
C(11)–C(12)–C(13)	122.2(13)	C(21)–C(22)–C(23)	120.6(13)
C(12)–C(13)–C(14)	120.7(14)	C(22)–C(23)–C(24)	121.7(15)
C(13)–C(14)–C(15)	118.3(14)	C(23)–C(24)–C(25)	119.9(16)
C(14)–C(15)–C(16)	122.8(14)	C(24)–C(25)–C(26)	118.9(16)
C(15)–C(16)–C(11)	119.9(13)	C(25)–C(26)–C(21)	121.5(14)
C(32)–C(31)–C(36)	119.8(12)	C(33)–C(34)–C(35)	121.3(15)
C(31)–C(32)–C(33)	119.7(13)	C(34)–C(35)–C(36)	116.8(14)
C(32)–C(33)–C(34)	121.0(15)	C(35)–C(36)–C(31)	121.5(13)
C(42)–C(41)–C(46)	118.1(12)	C(52)–C(51)–C(56)	119.7(12)
C(41)–C(42)–C(43)	118.9(13)	C(51)–C(52)–C(53)	117.9(13)
C(42)–C(43)–C(44)	119.2(14)	C(52)–C(53)–C(54)	120.6(15)
C(43)–C(44)–C(45)	123.3(15)	C(53)–C(54)–C(55)	124.2(16)
C(44)–C(45)–C(46)	117.1(14)	C(54)–C(55)–C(56)	115.5(15)
C(45)–C(46)–C(41)	123.3(13)	C(55)–C(56)–C(51)	121.7(14)
C(62)–C(61)–C(66)	117.5(12)	C(63)–C(64)–C(65)	122.3(14)
C(61)–C(62)–C(63)	119.9(12)	C(64)–C(65)–C(66)	118.4(13)
C(62)–C(63)–C(64)	120.4(14)	C(65)–C(66)–C(61)	121.4(12)

^a "Cent" is the midpoint of the triple bond, C(5)–C(6).

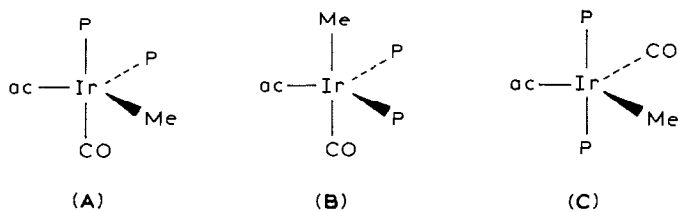


Fig. 3. Possible structures for the kinetic isomer with the assumption that $C_2(CO_2Me)_2$ remains in an equatorial position (ac = $C_2(CO_2Me)_2$, P = PPh_3).

steric repulsion between the "C(5)-end" of the $C_2(CO_2Me)_2$ ligand and the equatorial PPh_3 group as opposed to that between the "C(6)-end" of the $C_2(CO_2Me)_2$ ligand and the CO ligand. The Ir–C_{ent} distance is 1.986 Å and the acetylenic C(5)–C(6) linkage is expanded from ~1.20 to 1.290(23) upon coordination to the iridium(I) center. The acetylenic ligand has the *cis*-bent configuration, with C(4)–C(5)–C(6) 143.0(15) and C(5)–C(6)–C(7) 143.0(15)°. These values are all in accord with the accepted mode of acetylene–metal bonding, composed of $\pi(\text{acetylene}) \rightarrow \text{metal}$ forward donation and $\text{metal} \rightarrow \text{acetylene} (d_\pi \rightarrow \pi^*)$ back donation. (The observed $\nu(C\equiv C)$ is 1781 cm^{-1} .)

The equatorial iridium–carbonyl distance (Ir–C(1) 1.812(15) Å) is almost 0.4 Å shorter than the iridium–methyl distance (Ir–C(2) 2.193(14) Å). Each of these is in good agreement with previously determined measurements. Thus, the Ir–Me distance can be compared with values of 2.202(22) Å in $(C_8H_{12})(PPhMe_2)_2IrMe$ [19] 2.153(18) Å in $(C_8H_{12})[Ph_2P(CH_2)_3PPh_2]IrMe$ [20] and 2.133(16) Å in $(C_8H_{12})[Ph_2P(CH_2)_2PPh_2]IrMe$ [21]; each of these trigonal bipyramidal molecules also has the methyl ligand in an axial coordination site. Shapley and Osborn [22] have reviewed site preferences in fluxional pentacoordinate transition metal complexes and concluded that (in the absence of steric effects) ligands which are strong π -acceptors will preferentially take up equatorial sites and those which are strong

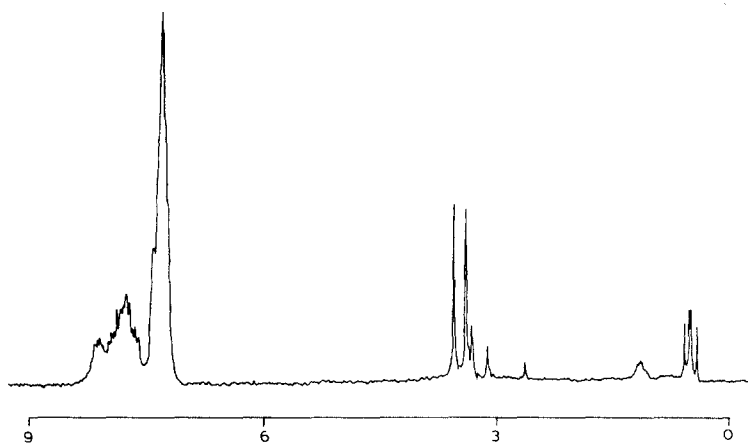


Fig. 4. NMR spectrum benzene- d_6 of the thermodynamic isomer of $MeIr(CO)(PPh_3)_2[C_2(CO_2Me)_2]$.

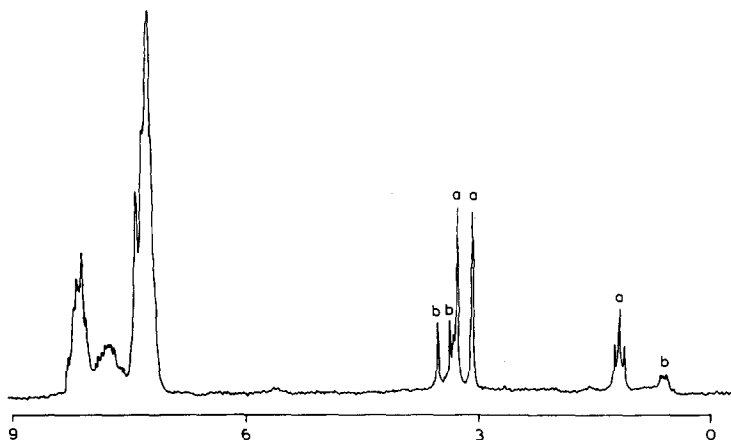


Fig. 5. NMR spectrum (-20°C , toluene- d_8) of the kinetic isomer of $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$. The resonances (a) are from the kinetic isomer while those marked (b) are from the thermodynamic isomer.

σ -donors will preferentially take up axial sites in trigonal-bipyramidal d^8 structures. Calculations by Rossi and Hoffmann are in agreement with this conclusion [23]. The thermodynamic isomer fully conforms to the Shapley–Osborn preference rules.

Under the assumption that the acetylene occupies an equatorial site, there are three possibilities for the structure of the kinetic isomer (Fig. 3). Structure **A** is readily derived from the thermodynamic isomer by a pseudorotation holding the acetylene in the equatorial position. Structure **B** is derived by addition of the acetylene to *trans*- $\text{MeIr}(\text{CO})(\text{PPh}_3)_2$ with a bending down of the PPh_3 groups. Such a structure is adopted by an olefin adduct of *trans*- $\text{MeIr}(\text{CO})(\text{PPh}_3)_2$ [24]. Structure **C** arises by bending of the CO and CH_3 groups toward each other upon addition of acetylene. The NMR (^1H) spectra of both isomers are shown in Figs. 4 and 5. The NMR spectrum indicates equivalent PPh_3 groups (CH_3 is triplet) (confirmed by ^{31}P NMR data) and inequivalent OCH_3 groups (two singlets). Only structure **C** is consistent with the NMR spectral data.

Pentacoordinate species are often stereochemically non-rigid with very low activation barriers. The barrier for interconversion between the kinetic and thermodynamic isomer of $\text{MeIr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CO}_2\text{Me})_2]$ must be at least 20–25 kcal/mol. While we have no direct mechanistic information on the interconversion, we note that several Berry-pseudorotations are required to convert between the two.

Supplementary Material Available

Tables of observed and calculated structure factors (15 pages) are available upon request from M.R.C.

Acknowledgment

We acknowledge the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. J.D.A. acknowledges the Alfred P. Sloan Foundation for a

fellowship. W.M.R. acknowledges the Graduate School of SUNY for a fellowship. A loan of $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ was generously provided by Johnson Matthey Corp.

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- 17 Discrepancy indices are defined as follows.

$$R_F (\%) = 100 \sum ||F_o| - |F_c|| / \sum |F_o|;$$

$$R_{wF} (\%) = 100 [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2};$$

$$GOF = [\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2},$$
 where NO = number of observations and NV = number of parameters varied.
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