Journal of Organometallic Chemistry, 301 (1986) 99–108
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FORMATION AND CRYSTAL STRUCTURE OF $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$. COMPARISON OF THE STRUCTURES OF ANALOGOUS ALKENE AND ALKYNE COMPLEXES

MELVYN ROWEN CHURCHILL, JAMES C. FETTINGER, WAYNE M. REES
and JIM D. ATWOOD

Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York 14214 (U.S.A.)

(Received July 30th, 1985)

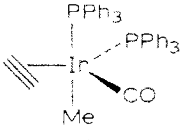
Summary

The complex $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$, synthesized from *trans*-$MeIr(CO)(PPh_3)_2$ and dimethyl maleate, crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ with a 13.997(5), b 17.878(5), c 15.709(4) Å, β 91.00(2)°, V 3930(2) Å^3 and $Z = 4$. X-ray data (Mo-K_α, 2θ 4.5–45.0°) were collected with a Syntex P2_1 automated four-circle diffractometer; the structure was solved and converged with R 5.5% for all 5069 unique reflections and R 4.3% for those 4343 data with $|F_o| > 3\sigma(|F_o|)$. The iridium(I) center has a distorted trigonal bipyramidal geometry with the Me and CO ligands occupying axial sites (Ir–Me(1) 2.159(8), Ir–CO 1.907(8) Å). The $MeCO_2CH{=}CHCO_2Me$ ligand is bonded in η^2 fashion to the iridium, with its coordinated double bond parallel to the equatorial plane. Bonds to the equatorial ligands are Ir–P(1) 2.344(2), Ir–P(2) 2.376(2) and Ir–(center of olefin) 2.017 Å. The observed ligand configuration is different from that for $MeIr(CO)(PPh_3)_2(MeCO_2C{\equiv}CCO_2Me)$ which has axial Me and PPh_3 ligands in its thermodynamically stable isomer.

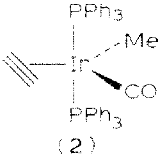
Introduction

We have previously reported a convenient synthesis of $MeIr(CO)(PPh_3)_2$, along with its addition reactions with various small molecules [1]. The alkyne complex, $MeIr(CO)(PPh_3)_2(MeCO_2C{\equiv}CCO_2Me)$, has been studied in detail [2]; a crystal structure shows the thermodynamically stable form to have structure **1**, whereas the kinetic isomer is believed (on spectroscopic grounds) to have structure **2**.

We now report the results of a single-crystal X-ray diffraction study on the closely-related alkene derivative, $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$.



(1)



(2)

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 Jeolco FX 90Q. *trans*-$Ir(PPh_3)_2(CO)Cl$ was prepared as previously described [3]. The CO stretching frequency is 1955 cm^{-1}. *trans*-$MeIr(CO)(PPh_3)_2$ is prepared by the addition of MeLi to *trans*-$Ir(CO)(PPh_3)_2Cl$ by the previously reported procedure [1]. The CO stretching frequency (1937 cm^{-1}) and ^1H NMR (0.63(t) δ, J(P–H) 9.0 Hz; 7.1(m) δ) are consistent with the formulation.

Preparation of $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$

In an inert atmosphere glove box, 0.25 ml of dimethyl maleate is added with stirring to a suspension of 0.20 g *trans*-$MeIr(CO)(PPh_3)_2$ in 15 ml benzene. The resulting pale yellow solution is left open in the inert atmosphere glove box for several days. Evaporation produces colorless crystals which can be washed with a small volume of C_6H_6 (1 ml), then with several ml of 3/1 benzene/hexane. Microanalysis: Found: C, 58.27; H, 4.55; P, 6.65. $C_{44}H_{41}IrO_5P_2$ calcd.: C, 58.46; H, 4.54; P, 6.87%. The carbonyl stretch (KBr) is at 1998 cm^{-1}. The NMR spectrum (benzene-d_6) is 0.23 (t, J(P–H) 8.7 Hz), 3.04(s), 3.50(s), 7.0(m) ppm.

Collection of X-ray diffraction data

An opaque colorless crystal of approximate dimensions $0.1 \times 0.1 \times 0.1$ mm^3 was sealed (under an argon atmosphere) in a thin-walled glass capillary which was inserted into a brass "pin" on a eucentric goniometer and centered on a Syntex $P2_1$ automated four-circle diffractometer. The subsequent determination of unit cell dimensions, crystal orientation matrix and Bravais lattice were carried out as described previously [4]; intensity data were collected via the coupled θ(crystal)–2θ(counter) method using conditions described in Table 1. The resulting data were corrected for the effects of absorption and for Lorentz and polarization effects. The diffraction symmetry is $2/m$ (C_{2h}); with the systematic absences of $h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$, the crystal is uniquely assigned to the centrosymmetric monoclinic space group $P2_1/n$ (No. 14). Any reflection with $I_0 < 0$ was assigned the value $|F_0| = 0$. Data were placed on an approximately absolute scale by means of a Wilson plot.

Solution and refinement of the structure

All subsequent calculations were performed using our locally-modified version of the Syntex XTL interactive crystallographic program package [5]. Throughout the

TABLE 1

CRYSTALLOGRAPHIC DATA FOR $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$

(A) Unit cell parameters at 24°C (297 K)

Crystal system: monoclinic
Space group: $P2_1/n$ (No. 14)
a 13.997(5) Å
b 17.878(5) Å
c 15.709(4) Å
β 91.00(2)°
V 3930(2) Å^3
$Z = 4$
Formula $C_{44}H_{41}IrO_5P_2$
Molec wt 903.99
D(calc'd) 1.53 g cm^{-3}
μ(Mo-K_α) 37.3 cm^{-1}

(B) Collection of intensity data

Diffractometer: Syntex $P2_1$
Radiation: Mo-K_α ($\bar{\lambda}$ 0.710730 Å)
Monchromator: pyrolytic graphite, 2θ(m) 12.160° for 002 reflection; equatorial mode, assumed 50% perfect and 50% ideally mosaic for polarization corrections
Reflections measured: $+h$, $+k$, $\pm l$ for $2\theta = 4.5$–45.0°, yielding 5069 unique data
Scan-type: coupled θ(crystal)–2θ(counter) at a scan-speed of 2.00 deg/min in 2θ over a range from $[2\theta(K_{\alpha_1})-1.0] \rightarrow [2\theta(K_{\alpha_2})+1.0]$ deg.
Backgrounds: stationary crystal and counter; recorded at each end of the 2θ scan (each for one-half of total scan time)
Standards: 3 approximately mutually orthogonal reflections were remeasured after each batch of 97 reflections; no significant fluctuations nor decay were observed
Absorption corrections: empirical, by interpolation in 2θ and ϕ between ψ-scans of a series of close-to-axial reflections

analysis, the calculated structure factors were based upon the analytical expression for the neutral atoms' scattering factors [6a]; corrections were made for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [6b] for all atoms. The function minimized during least-squares procedures was $\Sigma w(|F_0| - |F_c|)^2$ where $1/w = [\sigma(|F_0|)]^2 + [0.015|F_0|]^2$. Discrepancy indices used below are defined in equations 1–3; here, NO is the number of observations and NV is the number of variables.

$$R_F(\%) = 100\Sigma||F_0| - |F_c||/\Sigma|F_0| \qquad (1)$$

$$R_{wF}(\%) = 100\left[\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|\right]^{1/2} \qquad (2)$$

$$\mathrm{GOF} = \left[\Sigma w(|F_0| - |F_c|)^2/(NO - NV)\right]^{1/2} \qquad (3)$$

The position of the iridium atom was quickly determined from a three-dimensional Patterson synthesis. All non-hydrogen atoms were immediately located from a difference-Fourier synthesis. Hydrogen atoms of the sp^2-carbons were included in calculated positions and methyl hydrogens were placed in the direction of their observed positions, each with the idealized C–H distance of 0.95 Å [7]. Refinement converged with R_F 5.5%, R_{wF} 4.6% and GOF 1.68 for all 5069 unique data (none rejected). The discrepancy indices for those 4343 data with $|F_0| > 3\sigma(|F_0|)$ were R_F 4.3% and R_{wF} 4.5%.

A final difference-Fourier map showed no remaining significant features; the structure is thus both correct and complete. Final positional and thermal parameters are collected in Tables 2 and 3.

TABLE 2

FINAL POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR MeIr(CO)-$(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$

Atom	x	y	z	B
Ir	0.19026(2)	0.19453(2)	0.08849(2)	
P(1)	0.31636(13)	0.11610(11)	0.04942(12)	
P(2)	0.14988(14)	0.27903(11)	−0.02317(13)	
C(11)	0.29118(51)	0.04437(40)	−0.03168(45)	2.54(14)
C(12)	0.34288(55)	0.03992(45)	−0.10672(50)	3.33(16)
C(13)	0.31762(62)	−0.01448(50)	−0.16806(55)	4.23(19)
C(14)	0.24335(64)	−0.06253(51)	−0.15481(58)	4.55(20)
C(15)	0.19246(59)	−0.05815(47)	−0.08122(53)	3.86(17)
C(16)	0.21631(56)	−0.00498(44)	−0.01949(50)	3.30(16)
C(21)	0.42328(49)	0.16233(40)	0.01024(44)	2.26(13)
C(22)	0.41130(58)	0.22320(45)	−0.04465(51)	3.42(16)
C(23)	0.48799(61)	0.26132(48)	−0.07650(54)	3.81(17)
C(24)	0.58047(60)	0.23965(48)	−0.05408(54)	3.84(17)
C(25)	0.59316(58)	0.17957(45)	−0.00099(52)	3.56(17)
C(26)	0.51563(52)	0.14005(41)	0.03075(46)	2.77(15)
C(31)	0.36530(50)	0.05777(40)	0.13761(46)	2.56(14)
C(32)	0.38112(56)	−0.01766(45)	0.12714(51)	3.47(16)
C(33)	0.41820(64)	−0.06050(51)	0.19436(58)	4.50(20)
C(34)	0.43973(64)	−0.02862(52)	0.27069(58)	4.57(20)
C(35)	0.42431(64)	0.04663(53)	0.28227(58)	4.61(20)
C(36)	0.38786(56)	0.09028(46)	0.21561(51)	3.58(17)
C(41)	0.22158(59)	0.36412(46)	−0.03155(53)	3.61(17)
C(42)	0.22947(64)	0.41074(53)	0.03956(58)	4.72(20)
C(43)	0.29479(80)	0.47271(63)	0.03649(72)	6.53(26)
C(44)	0.34595(86)	0.48195(70)	−0.03176(83)	7.37(29)
C(45)	0.34222(85)	0.44039(72)	−0.10010(78)	7.38(30)
C(46)	0.27730(67)	0.37819(54)	−0.10215(59)	4.83(21)
C(51)	0.13993(53)	0.24497(42)	−0.13343(48)	2.84(15)
C(52)	0.10517(69)	0.29145(52)	−0.19710(62)	5.01(21)
C(53)	0.08810(75)	0.26298(62)	−0.27931(68)	5.92(24)
C(54)	0.10582(73)	0.19100(59)	−0.29688(65)	5.60(22)
C(55)	0.14163(64)	0.14377(50)	−0.23530(58)	4.38(19)
C(56)	0.15779(55)	0.17097(42)	−0.15352(50)	3.14(16)
C(61)	0.02536(53)	0.31310(43)	−0.01497(48)	3.06(15)
C(62)	−0.04648(73)	0.26331(57)	−0.03824(63)	5.22(22)
C(63)	−0.14420(85)	0.28400(64)	−0.03747(74)	6.66(27)
C(64)	−0.16451(75)	0.35447(61)	−0.00782(67)	5.89(24)
C(65)	−0.09701(67)	0.40384(54)	0.01669(59)	4.82(20)
C(66)	−0.00053(60)	0.38322(47)	0.01167(53)	3.80(17)
C(7)	0.09229(58)	0.12856(45)	0.04837(50)	3.13(16)
O(7)	0.03350(37)	0.09204(34)	0.02007(37)	
Me(1)	0.29998(57)	0.26833(46)	0.13800(51)	3.40(16)
C(101)	0.12759(65)	0.09758(52)	0.25045(60)	
C(102)	0.17047(56)	0.16855(45)	0.21936(51)	
C(103)	0.11040(56)	0.23180(44)	0.19667(48)	
C(104)	0.00621(56)	0.22522(47)	0.19569(50)	
O(1)	0.10375(58)	0.09018(39)	0.32310(43)	
O(2)	0.12073(47)	0.04270(34)	0.19379(41)	
O(3)	−0.04009(40)	0.16823(33)	0.19074(40)	
O(4)	−0.03525(40)	0.29312(31)	0.20297(40)	
Me(4)	−0.13773(65)	0.29438(54)	0.20627(67)	
Me(2)	0.0748(10)	−0.02509(66)	0.22043(81)	

TABLE 2 (continued)

Atom	x	y	z	B
H(12)	0.3908	0.0789	-0.1023	6.0
H(13)	0.3524	-0.0180	-0.2202	6.0
H(14)	0.2254	-0.0997	-0.1971	6.0
H(15)	0.1392	-0.0920	-0.0726	6.0
H(16)	0.1808	-0.0027	0.0333	6.0
H(22)	0.3477	0.2390	-0.0594	6.0
H(23)	0.4767	0.3029	-0.1154	6.0
H(24)	0.6352	0.2661	-0.0755	6.0
H(25)	0.6571	0.1641	0.0159	6.0
H(26)	0.5252	0.0971	0.0668	6.0
H(32)	0.3661	-0.0407	0.0725	6.0
H(33)	0.4296	-0.1138	0.1854	6.0
H(34)	0.4654	-0.0590	0.3172	6.0
H(35)	0.4373	0.0702	0.3374	6.0
H(36)	0.3770	0.1435	0.2238	6.0
H(42)	0.1914	0.3998	0.0906	6.0
H(43)	0.2992	0.5094	0.0843	6.0
H(44)	0.3911	0.5233	-0.0318	6.0
H(45)	0.3840	0.4508	-0.1471	6.0
H(46)	0.2701	0.3462	-0.1530	6.0
H(52)	0.0934	0.3445	-0.1830	6.0
H(53)	0.0649	0.2954	-0.3237	6.0
H(54)	0.0933	0.1707	-0.3532	6.0
H(55)	0.1578	0.0925	-0.2476	6.0
H(56)	0.1816	0.1373	-0.1093	6.0
H(62)	-0.0276	0.2129	-0.0522	6.0
H(63)	-0.1948	0.2497	-0.0572	6.0
H(64)	-0.2316	0.3708	-0.0040	6.0
H(65)	-0.1131	0.4540	0.0367	6.0
H(66)	0.0493	0.4187	0.0275	6.0
H(102)	0.2394	0.1722	0.2146	6.0
H(103)	0.1399	0.2793	0.1822	6.0
H(M1A)	0.2726	0.3120	0.1616	6.0
H(M2A)	0.0725	-0.0615	0.1758	6.0
H(M4A)	-0.1604	0.3439	0.2119	6.0
H(M1B)	0.3376	0.2435	0.1806	6.0
H(M1C)	0.3418	0.2832	0.0929	6.0
H(M2B)	0.1069	-0.0466	0.2687	6.0
H(M2C)	0.0094	-0.0151	0.2364	6.0
H(M4B)	-0.1656	0.2716	0.1575	6.0
H(M4C)	-0.1582	0.2663	0.2560	6.0

Description of the molecular structure

The crystal contains an ordered arrangement of discrete molecular units of $\mathrm{MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)}$ separated by normal Van der Waals' distances; there are no abnormally short intermolecular contacts. The overall molecular geometry and the atomic labelling scheme are illustrated in Fig. 1; a stereoscopic view of the molecule is provided by Fig. 2. Interatomic distances and angles are collected in Tables 4 and 5.

The central iridium(I) atom has a coordination geometry which may be regarded as a slightly distorted trigonal bipyramid. Within the framework of this description

TABLE 3

ANISOTROPIC THERMAL PARAMETERS [a] FOR $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ir	1.864(13)	2.505(14)	2.259(14)	0.121(13)	−0.1193(84)	−0.209(13)
P(1)	2.066(84)	2.710(87)	2.248(84)	0.116(70)	−0.242(65)	−0.107(69)
P(2)	2.294(88)	2.996(91)	2.964(93)	0.360(72)	−0.317(70)	0.176(75)
O(7)	2.83(26)	4.87(31)	5.53(33)	−0.96(25)	−0.05(23)	−1.30(27)
C(101)	5.02(50)	4.23(48)	3.93(48)	1.39(40)	0.96(38)	0.81(41)
C(102)	3.06(39)	3.77(40)	3.32(39)	0.17(32)	0.98(31)	−0.02(32)
C(103)	3.18(39)	3.36(37)	2.74(36)	−0.04(33)	0.70(29)	−0.62(30)
C(104)	2.86(39)	3.31(39)	3.26(39)	0.41(35)	0.55(30)	−0.75(32)
O(1)	11.40(56)	5.80(39)	4.42(36)	1.97(39)	2.72(36)	2.16(32)
O(2)	6.54(38)	3.84(30)	5.31(36)	−0.82(29)	0.95(29)	0.36(28)
O(3)	3.47(30)	3.73(30)	6.32(37)	−0.14(25)	0.48(25)	−1.11(26)
O(4)	3.31(27)	3.76(31)	6.24(35)	0.65(23)	1.72(24)	−0.11(25)
Me(4)	3.68(46)	5.36(55)	7.06(60)	1.35(41)	1.55(41)	0.84(46)
Me(2)	13.3(11)	5.90(65)	8.16(81)	−3.89(69)	2.02(73)	1.18(59)

[a] The anisotropic thermal parameters are in standard Syntex XTL format and enter the expression for the calculated structure factor in the form:

$$\exp\left[-0.25\left(h^2a^{*2}B_{11}+\ldots 2hka^*b^*B_{12}+\ldots\right)\right]$$

the methyl group (centered on Me(1)) and the carbonyl ligand (C(7)–O(7)) occupy axial sites with < C(7)–Ir–Me(1) 178.19(32)°. The two triphenylphosphine ligands and the alkene ligand (with "Cent" being the midpoint of the olefinic linkage) occupy equatorial sites, with angles P(1)–Ir–P(2) 110.95(7)°, P(1)–Ir–Cent 123.22° and P(2)–Ir–Cent 125.02°. The axial–equatorial angles are all in the range 83–95°.

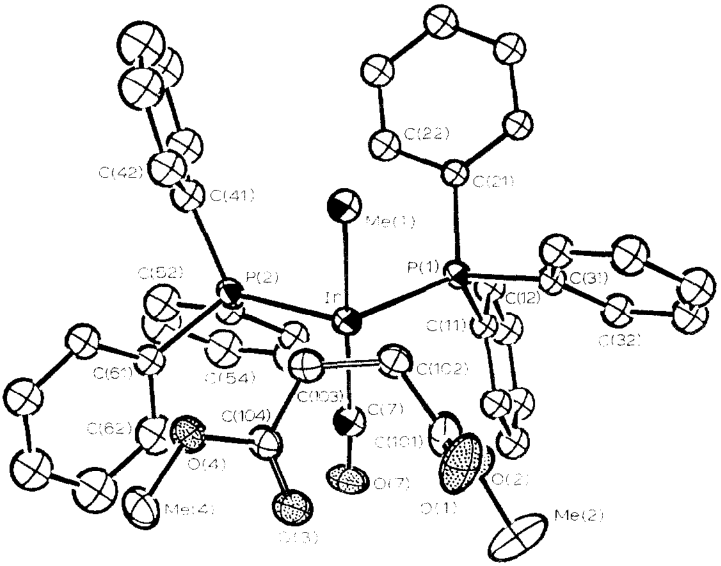


Fig. 1. Molecular geometry and labelling of atoms in the $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$ molecule, showing the trigonal bipyramidal geometry about the iridium(I) atom [ORTEP-II diagram].

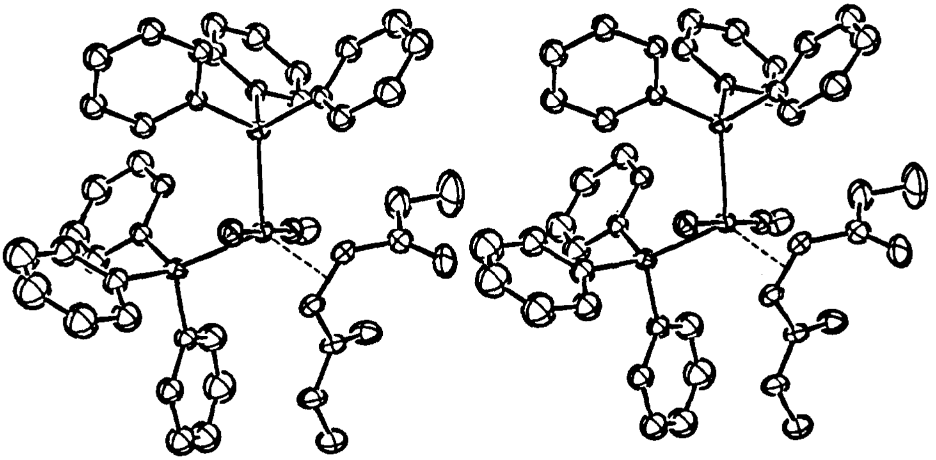


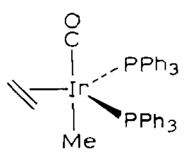
Fig. 2. Stereoview of the MeIr(CO)$(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$ molecule, projected onto a plane about 10° from the true equatorial coordination plane.

Angles from the carbonyl ligand are mainly obtuse: P(1)–Ir–C(7) 94.81(24)°, P(2)–Ir–C(7) 89.35(24)° and C(7)–Ir–Cent 94.61°; those from the methyl group are smaller, with P(1)–Ir–Me(1) 85.74(22)°, P(2)–Ir–Me(1) 92.06(22)° and Me(1)–Ir–Cent 83.65°. The equatorial coordination plane (defined by P(1), P(2) and "Cent") has the equation: $-0.6894X - 0.6620Y - 0.2941Z + 4.6458 = 0$. The iridium(I) atom lies +0.1157(3) Å from this plane, while the equatorial ligands are +2.020(8) Å (C(7)) and −2.036(8) Å (Me(1)) from the plane.

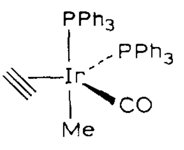
The equatorial alkene ligand is in a "parallel" configuration with an η^2 face-on orientation. The iridium–carbon distances are Ir–C(102) 2.130(8) Å and Ir–C(103) 2.156(8) Å, with Ir–Cent 2.017 Å. The initial C=C bond is lengthened from ~ 1.34 Å in an uncoordinated olefin to C(102)–C(103) 1.450(11) Å in the present molecule.

The axial iridium–carbonyl bond (Ir–C(7) 1.907(8) Å) is some 0.25 Å shorter than the *trans*-iridium–methyl linkage (Ir–Me(1) 2.159(8) Å). The iridium–methyl linkage may be compared with other axial Ir–Me linkages in trigonal bipyramidal molecules: 2.133(16) Å in (cyclo-C_8H_{12})($Ph_2P(CH_2)_2PPh_2$)IrMe [8], 2.153(18) Å in (cyclo-C_8H_{12})($Ph_2P(CH_2)_3PPh_2$)IrMe [9], 2.193(4) Å in MeIr(CO)$(PPh_3)_2(MeCO_2$-$C{\equiv}CCO_2Me)$ [2] and 2.202(22) in (cyclo-C_8H_{12})$(PPhMe_2)_2$IrMe [10].

The present molecule differs from the thermodynamically stable isomer of the acetylene analogue in that the axial ligands are now Me and CO, rather than Me and PPh_3 (cf **3** and **4**, below).



(3)



(4)

In each case, however, the strongly σ-donating methyl group is in an axial site. This is consistent with the observations of Shapley and Osborn [11], Churchill and

TABLE 4

INTERATOMIC DISTANCES (in Å) FOR $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$

(A) Iridium–ligand distances			
Ir–P(1)	2.344(2)	Ir–Me(1)	2.159(8)
Ir–P(2)	2.376(2)	Ir–C(102)	2.130(8)
Ir–C(7)	1.907(8)	Ir–C(103)	2.156(8)
C(7)–O(7)	1.135(10)	Ir–Cent [a]	2.017
(B) Phosphorus–carbon distances			
P(1)–C(11)	1.837(7)	P(2)–C(41)	1.829(8)
P(1)–C(21)	1.826(7)	P(2)–C(51)	1.839(8)
P(1)–C(31)	1.855(7)	P(2)–C(61)	1.853(8)
(C) Distances within the $MeCO_2CH{=}CHCO_2Me$ *ligand*			
C(101)–O(1)	1.202(12)	C(104)–O(3)	1.209(10)
C(101)–O(2)	1.327(11)	C(104)–O(4)	1.351(10)
O(2)–Me(2)	1.437(14)	O(4)–Me(4)	1.436(11)
C(101)–C(102)	1.490(12)	C(103)–C(104)	1.463(11)
C(102)–C(103)	1.450(11)		
(D) C–C distances in PPh_3 *ligands*			
C(11)–C(12)	1.396(11)	C(41)–C(42)	1.396(12)
C(12)–C(13)	1.410(12)	C(42)–C(43)	1.438(15)
C(13)–C(14)	1.367(13)	C(43)–C(44)	1.310(17)
C(14)–C(15)	1.371(12)	C(44)–C(45)	1.306(18)
C(15)–C(16)	1.394(11)	C(45)–C(46)	1.436(16)
C(16)–C(11)	1.386(11)	C(46)–C(41)	1.390(12)
C(21)–C(22)	1.397(11)	C(51)–C(52)	1.382(12)
C(22)–C(23)	1.373(12)	C(52)–C(53)	1.405(14)
C(23)–C(24)	1.391(12)	C(53)–C(54)	1.340(15)
C(24)–C(25)	1.369(12)	C(54)–C(55)	1.372(14)
C(25)–C(26)	1.394(11)	C(55)–C(56)	1.389(12)
C(26)–C(21)	1.385(10)	C(56)–C(51)	1.384(11)
C(31)–C(32)	1.377(11)	C(61)–C(62)	1.387(13)
C(32)–C(33)	1.397(12)	C(62)–C(63)	1.417(16)
C(33)–C(34)	1.357(13)	C(63)–C(64)	1.375(16)
C(34)–C(35)	1.375(13)	C(64)–C(65)	1.344(14)
C(35)–C(36)	1.395(12)	C(65)–C(66)	1.403(13)
C(36)–C(31)	1.388(11)	C(66)–C(61)	1.372(11)

[a] Cent is the midpoint of the C(102)–C(103) bond.

Lin [12] and Goldfield and Raymond [13] that strong σ-donors occupy axial positions, while strong π-acceptors occupy equatorial sites. A theoretical treatment confirming these generalizations has been presented by Rossi and Hoffmann [14]. The axial carbonyl ligand in $MeIr(CO)(PPh_3)_2(MeCO_2CH{=}CHCO_2Me)$ vis à vis the axial PPh_3 group in $MeIr(CO)(PPh_3)_2(MeCO_2C{\equiv}CCO_2Me)$ presumably results to reduce steric interactions within the molecule.

The alkene and alkyne ligands appear to be bound with about the same bond strength as indicated by Ir–C distances (Ir–C(alkene) 2.143 Å (aver) and Ir–C(alkyne) 2.088 Å (aver)) and C–C distances (C=C(coordinated) 1.450(11) Å, increased by ~ 0.11 Å from an uncoordinated double bond; C≡C(coordinated) 1.290(23) Å, increased by ~ 0.09 Å from an uncoordinated triple bond). Ir–PPh_3 distances are shorter in the alkene complex (2.344(2) and 2.376(2) Å than in the alkyne complex

TABLE 5

INTERATOMIC ANGLES (in deg.) FOR MeIr(CO)(PPh$_3$)$_2$(MeCO$_2$CH=CHCO$_2$Me)

(A) Angles about the iridium atom			
P(1)–Ir–P(2)	110.95(7)	C(7)–Ir–Me(1)	178.19(32)
P(1)–Ir–C(7)	94.81(24)	C(7)–Ir–Cent	94.61
P(1)–Ir–Me(1)	85.74(22)	Me(1)–Ir–Cent	83.65
P(1)–Ir–Cent	123.22	C(7)–Ir–C(102)	94.55(32)
P(2)–Ir–C(7)	89.35(24)	C(7)–Ir–C(103)	94.13(32)
P(2)–Ir–Me(1)	92.06(22)	Me(1)–Ir–C(102)	83.64(30)
P(2)–Ir–Cent	125.02	Me(1)–Ir–C(103)	84.41(30)
		C(102)–Ir–C(103)	39.54(30)
(B) Ir–P–C and C–P–C angles			
Ir–P(1)–C(11)	117.56(24)	C(11)–P(1)–C(21)	103.33(32)
Ir–P(1)–C(21)	116.29(24)	C(11)–P(1)–C(31)	100.91(32)
Ir–P(1)–C(31)	114.23(24)	C(21)–P(1)–C(31)	102.24(32)
Ir–P(2)–C(41)	117.28(27)	C(41)–P(2)–C(51)	103.90(36)
Ir–P(2)–C(51)	119.87(25)	C(41)–P(2)–C(61)	104.45(36)
Ir–P(2)–C(61)	111.70(25)	C(51)–P(2)–C(61)	96.80(34)
(C) Ir–C–O angle			
Ir–C(7)–O(7)	175.7(7)		
(D) Angles within the MeCO$_2$CH=CHCO$_2$Me ligand			
Me(2)–O(2)–C(101)	117.1(8)	Me(4)–O(4)–C(104)	116.6(7)
O(1)–C(101)–O(2)	122.5(9)	O(3)–C(104)–O(4)	122.1(7)
C(102)–C(101)–O(1)	121.7(8)	C(103)–C(104)–O(3)	127.0(8)
C(102)–C(101)–O(2)	115.8(8)	C(103)–C(104)–O(4)	110.9(7)
C(103)–C(102)–C(101)	120.6(7)	C(102)–C(103)–C(104)	120.9(7)
Ir–C(102)–C(101)	124.2(6)	Ir–C(103)–C(104)	119.8(5)
Ir–C(102)–C(103)	71.2(4)	Ir–C(103)–C(102)	69.3(4)
(E) P–C–C angles			
P(1)–C(11)–C(12)	122.0(6)	P(2)–C(41)–C(42)	118.3(6)
P(1)–C(11)–C(16)	119.0(6)	P(2)–C(41)–C(46)	121.6(7)
P(1)–C(21)–C(22)	118.1(6)	P(2)–C(51)–C(52)	120.2(6)
P(1)–C(21)–C(26)	123.9(5)	P(2)–C(51)–C(56)	121.4(6)
P(1)–C(31)–C(32)	121.3(6)	P(2)–C(61)–C(62)	116.7(6)
P(1)–C(31)–C(36)	120.0(6)	P(2)–C(61)–C(66)	125.1(6)
(F) C–C–C angles within PPh$_3$ ligands			
C(16)–C(11)–C(12)	119.0(7)	C(46)–C(41)–C(42)	119.5(8)
C(11)–C(12)–C(13)	119.3(7)	C(41)–C(42)–C(43)	118.3(9)
C(12)–C(13)–C(14)	120.8(8)	C(42)–C(43)–C(44)	118.8(10)
C(13)–C(14)–C(15)	120.0(8)	C(43)–C(44)–C(45)	125.9(12)
C(14)–C(15)–C(16)	120.3(8)	C(44)–C(45)–C(46)	118.4(11)
C(15)–C(16)–C(11)	120.7(7)	C(45)–C(46)–C(41)	119.1(9)
C(26)–C(21)–C(22)	118.0(7)	C(56)–C(51)–C(52)	118.2(7)
C(21)–C(22)–C(23)	121.7(7)	C(51)–C(52)–C(53)	120.0(9)
C(22)–C(23)–C(24)	120.0(8)	C(52)–C(53)–C(54)	120.5(10)
C(23)–C(24)–C(25)	118.9(8)	C(53)–C(54)–C(55)	120.8(10)
C(24)–C(25)–C(26)	121.5(7)	C(54)–C(55)–C(56)	119.2(8)
C(25)–C(26)–C(21)	120.0(7)	C(55)–C(56)–C(51)	121.2(7)
C(36)–C(31)–C(32)	118.8(7)	C(66)–C(61)–C(62)	118.2(8)
C(31)–C(32)–C(33)	120.3(7)	C(61)–C(62)–C(63)	121.7(9)
C(32)–C(33)–C(34)	120.8(8)	C(62)–C(63)–C(64)	116.6(10)
C(33)–C(34)–C(35)	119.7(9)	C(63)–C(64)–C(65)	123.4(10)
C(34)–C(35)–C(36)	120.3(8)	C(64)–C(65)–C(66)	118.9(9)
C(35)–C(36)–C(31)	120.2(8)	C(65)–C(66)–C(61)	121.1(8)

(2.402(3) and 2.425(4) Å); whether this arises from electronic binding preferences or merely reduced steric interactions (equatorial ··· equatorial versus axial ··· equatorial, respectively) cannot now be determined. Lastly, we note that the *axial* Ir–CO bond length of 1.907(8) Å in the alkene complex is significantly longer than the *equatorial* Ir–CO bond length of 1.812(15) Å in the alkyne complex; this is consistent with the reduced π-acceptor capabilities of the axial (relative to the equatorial) position in a trigonal bipyramidal system.

Supplementary material. A listing of observed and calculated structure factor amplitudes is available upon request from M.R.C.

Acknowledgment

We acknowledge the National Science Foundation and the Donors of the Petroleum Research Fund 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 $IrCl_3 \cdot xH_2O$ was generously provided by Johnson Matthey Corporation.

References

1 W.M. Rees, M.R. Churchill, Y.J. Li and J.D. Atwood, Organometallics, 4 (1985) 1162.
2 M.R. Churchill, W.M. Rees, J.C. Fettinger and J.D. Atwood, Organometallics, in press.
3 C.T. Sears and M. Kubota, Inorg. Synth., 11 (1968) 101.
4 M.R. Churchill, R.A. Lashewycz and F.J. Rotella, Inorg. Chem., 16 (1977) 265.
5 Syntex XTL Operations Manual, 2nd edition, Syntex Analytical Instruments, Inc., Cupertino, California (U.S.A.), 1976.
6 International Tables for X-Ray Diffraction, Volume 4, Kynoch Press, Birmingham, England, 1974 (a) pp. 99–101, (b) 149–150.
7 M.R. Churchill, Inorg. Chem., 12 (1973) 1213.
8 M.R. Churchill and S.A. Bezman, Inorg. Chem., 12 (1973) 260.
9 M.R. Churchill and S.A. Bezman, Inorg. Chem., 12 (1973) 531.
10 M.R. Churchill and S.A. Bezman, Inorg. Chem., 11 (1972) 2243.
11 J.R. Shapley and J.A. Osborn, Acc. Chem. Res., 6 (1973) 305.
12 M.R. Churchill and K.K.G. Lin, J. Am. Chem. Soc., 96 (1974) 76.
13 S.A. Goldfield and K.N. Raymond, Inorg. Chem., 13 (1974) 770.
14 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.