Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Roberts, P. & Sheldrick, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure of Dicarbonylbis-(μ-3,5-dimethylpyrazolyl)-bis(4-tolyl diphenylphosphinite)diiridium(I)–Dichloromethane (1/1)

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Abstract

In bis(μ-3,5-dimethylpyrazolyl-*N*:*N*′)-bis[carbonyl(4-tolyl diphenylphosphinite-*P*)iridium(I)] dichloromethane solvate, two Ir^{I} atoms are joined by two 3,5-dimethylpyrazolyl bridges with one carbonyl and one 4-tolyl diphenylphosphinite ligand completing the square-planar geometry about each Ir atom. The Ir···Ir distance of 3.307 (1) Å is greater than the distance of 3.22 Å found in a similar pyrazolyl-bridged iridium(I) dimer [Fox (1989). PhD dissertation, California Institute of Technology, USA].

Comment

The title compound $[Ir(\mu\text{-pz*})(CO)(Ph_2POC_6H_4CH_3)]_2$, where pz* is 3,5-dimethylpyrazolyl, was synthesized as a model complex for the study of electron transfer in iridium dimer/pyridinium donor–acceptor complexes (Ir_2-py^+). The photophysical and electrochemical data for this compound reveal energetic and kinetic parameters [$E_{00}(S_1)$ = 2.4, $E_{00}(T_1)$ = 1.9 eV, $E_{1/2}(Ir_2/Ir_2^+)$ = 0.4 V *versus* SSCE (sodium saturated calomel electrode), τ_S = 125 ps, τ_T = 1 μs] used in analyzing electron-transfer rates for the series of Ir_2-py^+ complexes. The synthesis of this compound is reported elsewhere (Farid, Chang, Winkler & Gray, 1993). Slow evaporation of a methylene chloride/acetonitrile solution produced acicular crystals.

The molecule exhibits approximate C_{2v} symmetry. The square-planar Ir atoms are almost identical and are coordinated to two adjacent dimethylpyrazolyl ligands with an average Ir—N distance of 2.077 [10] Å, where square brackets indicate a scatter e.s.d. A carbonyl ligand at 1.804 [9] Å and a tolyl diphenylphosphinite group with an Ir—P bond of 2.224 [0] Å complete the coordination shell about each Ir atom. The N—Ir—N angle is 84.1 [14]° and the other three angles about the Ir atom range from 91.4 [6] to 92.4 [4]°.

The bridging pyrazolyl groups retain the structure of the free ligand. The dihedral angle between the two pyrazolyl groups is 78.8 (6)°. The torsion angles Ir(1)—N(1)—N(2)—Ir(2) and Ir(1)—N(3)—N(4)—Ir(2)

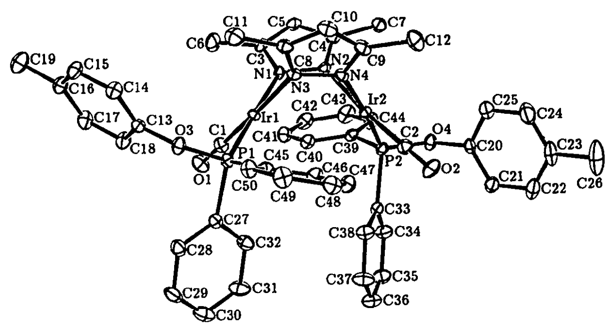

Fig. 1. An *ORTEP* view of the dimer with 15% probability ellipsoids. H atoms are not shown.

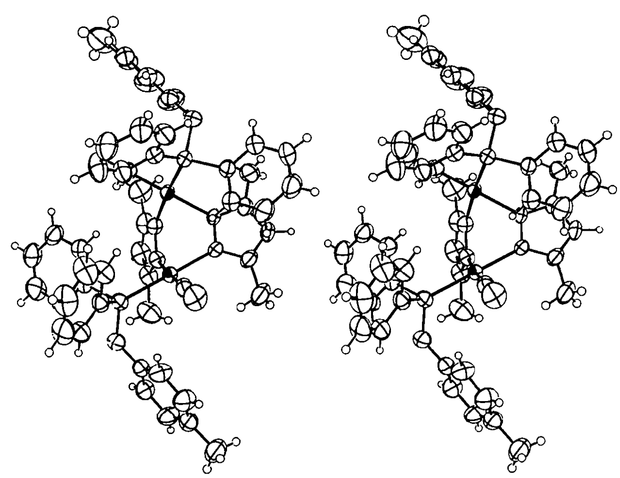

Fig. 2. An *ORTEP* stereoview of the iridium complex; atoms are drawn at the 50% probability level with H atoms at one tenth scale.

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are 12.1 (4) and 4.9 (4)°, respectively. The remaining ligand geometry is as expected. Substantial overlap of the aromatic rings occurs between neighboring molecules in the crystal. The population of the dichloromethane solvate refined to near unity [0.959 (4)].

The Ir···Ir solid-state non-bonding separation of 3.307 (1) Å is similar to the $M\cdots M$ separations in analogous bispyrazolyl-bridged Ir and Rh d^8–d^8 dimers. For six iridium compounds (Nussbaum, Rettig, Storr & Trotter, 1985; Beveridge, Bushnell & Stobart, 1983; Coleman, Eadie, Stobart, Zaworotko & Atwood, 1982; Beveridge, Bushnell, Dixon, Eadie, Stobart, Atwood & Zaworotko, 1982; Fox, 1989), the average Ir···Ir separation is 3.28 [12] Å (ranging from 3.162 to 3.506 Å); and for four rhodium compounds (Beveridge, Bushnell & Stobart, 1983; Louie, Rettig, Storr & Trotter, 1984; Uson, Oro, Ciriano, Pinillos, Tiripicchio & Carmellini, 1981), the average Rh···Rh separation is 3.31 [18] Å (ranging from 3.154 to 3.568 Å).

Experimental

Crystal data

$[Ir_2(C_5H_7N_2)_2(C_{19}H_{17}OP)_2-(CO)_2].CH_2Cl_2$	D_x = 1.69 Mg m^{-3}
M_r = 1300.28	Mo $K\alpha$ radiation
Monoclinic	λ = 0.71073 Å
$P2_1/c$	Cell parameters from 24 reflections
a = 18.677 (2) Å	θ = 15–16.5°
b = 13.817 (1) Å	μ = 5.391 mm^{-1}
c = 20.225 (3) Å	T = 293 K
β = 101.37 (1)°	Irregular
V = 5116.8 (10) Å^3	0.6 × 0.6 × 0.4 mm
Z = 4	Orange-red

Data collection

Enraf–Nonius CAD-4 diffractometer	6662 observed reflections
θ scans	θ_{max} = 22.5°
Absorption correction: by integration from crystal shape	h = −20 → 20
T_{min} = 0.39, T_{max} = 0.54	k = 0 → 14
14173 measured reflections	l = −21 → 21
6662 independent reflections	3 standard reflections frequency: 180 min intensity variation: 2%

Refinement

Refinement on F^2	$\Delta\rho_{min}$ = −0.64 e Å^{-3}
Final R = 0.0316	Extinction correction: Becker–Coppens type 1 isotropic
wR = 0.0025	Extinction coefficient: 0.092 (3)×10^{-6}
S = 1.46	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2*B*)
6662 reflections	
588 parameters	
H-atom parameters not refined	
Weighting scheme based on measured e.s.d.'s	
$(\Delta/\sigma)_{max}$ = 0.04	
$\Delta\rho_{max}$ = 0.78 e Å^{-3}	

Data collection: CAD-4 software (Schagen, Straver, van Meurs & Williams, 1989). Cell refinement: CAD-4 software. Data reduction: *CRYM* (Duchamp, 1964). Program(s) used to solve structure: *CRYM*. Program(s) used to refine structure: *CRYM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CRYM*.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir(1)	0.25396 (1)	0.05931 (1)	0.83242 (1)	0.0370 (1)
Ir(2)	0.22477 (1)	0.28327 (2)	0.87831 (1)	0.0384 (5)
P(1)	0.24573 (7)	−0.0576 (1)	0.90619 (1)	0.0438 (3)
P(2)	0.32749 (8)	0.3689 (1)	0.90235 (7)	0.0444 (3)
N(1)	0.2567 (2)	0.1699 (3)	0.7636 (2)	0.041 (1)
N(2)	0.2361 (2)	0.2607 (3)	0.7798 (2)	0.041 (1)
N(3)	0.1458 (2)	0.1024 (3)	0.8281 (2)	0.043 (1)
N(4)	0.1346 (2)	0.1941 (3)	0.8505 (2)	0.044 (1)
O(1)	0.4071 (2)	0.0045 (3)	0.8293 (2)	0.078 (1)
O(2)	0.1901 (3)	0.3201 (3)	1.0135 (2)	0.083 (1)
O(3)	0.2176 (2)	−0.1645 (3)	0.8786 (2)	0.058 (1)
O(4)	0.3235 (2)	0.4862 (2)	0.9104 (2)	0.056 (1)
C(1)	0.3465 (3)	0.0257 (4)	0.8308 (3)	0.055 (2)
C(2)	0.2050 (3)	0.3056 (4)	0.9610 (3)	0.058 (2)
C(3)	0.2700 (3)	0.1753 (4)	0.7005 (3)	0.053 (2)
C(4)	0.2360 (3)	0.3200 (4)	0.7278 (3)	0.052 (2)
C(5)	0.2577 (3)	0.2681 (4)	0.6771 (3)	0.057 (2)
C(6)	0.2934 (4)	0.0880 (5)	0.6668 (3)	0.088 (2)
C(7)	0.2126 (4)	0.4232 (4)	0.7305 (3)	0.073 (2)
C(8)	0.0811 (3)	0.0579 (4)	0.8120 (3)	0.055 (2)
C(9)	0.0631 (3)	0.2048 (5)	0.8470 (3)	0.059 (2)
C(10)	0.0281 (3)	0.1204 (5)	0.8231 (3)	0.070 (2)
C(11)	0.0745 (4)	−0.0424 (5)	0.7848 (4)	0.084 (2)
C(12)	0.0318 (4)	0.2971 (5)	0.8673 (4)	0.090 (2)
C(13)	0.2366 (3)	−0.2126 (4)	0.8231 (3)	0.051 (1)
C(14)	0.1824 (3)	−0.2647 (4)	0.7831 (3)	0.058 (2)
C(15)	0.1987 (3)	−0.3147 (4)	0.7288 (3)	0.066 (2)
C(16)	0.2668 (3)	−0.3135 (4)	0.7135 (3)	0.061 (2)
C(17)	0.3199 (3)	−0.2608 (5)	0.7550 (4)	0.073 (2)
C(18)	0.3057 (3)	−0.2108 (4)	0.8100 (3)	0.062 (2)
C(19)	0.2830 (4)	−0.3656 (5)	0.6525 (4)	0.090 (2)
C(20)	0.2791 (3)	0.5284 (4)	0.9511 (3)	0.052 (2)
C(21)	0.3087 (4)	0.5538 (4)	1.0151 (3)	0.066 (2)
C(22)	0.2653 (5)	0.5975 (5)	1.0548 (4)	0.086 (2)
C(23)	0.1932 (5)	0.6133 (5)	1.0303 (5)	0.090 (3)
C(24)	0.1649 (5)	0.5887 (6)	0.9652 (5)	0.108 (3)
C(25)	0.2078 (4)	0.5465 (5)	0.9249 (4)	0.088 (2)
C(26)	0.1439 (6)	0.6554 (6)	1.0748 (6)	0.162 (4)
C(27)	0.3285 (3)	−0.0854 (4)	0.9670 (3)	0.049 (1)
C(28)	0.3455 (4)	−0.1792 (4)	0.9904 (3)	0.065 (2)
C(29)	0.4075 (4)	−0.1951 (5)	1.0400 (4)	0.083 (2)
C(30)	0.4508 (4)	−0.1209 (7)	1.0666 (4)	0.088 (2)
C(31)	0.4345 (4)	−0.0292 (6)	1.0445 (4)	0.083 (2)
C(32)	0.3739 (3)	−0.0111 (5)	0.9947 (3)	0.065 (2)
C(33)	0.3914 (3)	0.3350 (4)	0.9793 (3)	0.047 (1)
C(34)	0.4586 (3)	0.3813 (5)	0.9961 (3)	0.067 (2)
C(35)	0.5068 (3)	0.3585 (5)	1.0544 (3)	0.075 (2)
C(36)	0.4890 (4)	0.2900 (6)	1.0971 (3)	0.081 (2)
C(37)	0.4232 (4)	0.2420 (6)	1.0807 (3)	0.085 (2)
C(38)	0.3758 (3)	0.2641 (4)	1.0213 (3)	0.064 (2)
C(39)	0.3859 (3)	0.3707 (4)	0.8405 (2)	0.047 (1)
C(40)	0.4139 (3)	0.2828 (4)	0.8237 (3)	0.056 (2)
C(41)	0.4623 (3)	0.2792 (5)	0.7798 (3)	0.069 (2)
C(42)	0.4817 (4)	0.3639 (6)	0.7520 (3)	0.079 (2)
C(43)	0.4531 (4)	0.4502 (5)	0.7673 (4)	0.083 (2)
C(44)	0.4055 (4)	0.4555 (4)	0.8117 (3)	0.069 (2)
C(45)	0.1804 (3)	−0.0385 (4)	0.9609 (3)	0.044 (1)
C(46)	0.1787 (3)	0.0525 (4)	0.9900 (3)	0.060 (2)
C(47)	0.1326 (3)	0.0710 (5)	1.0341 (3)	0.066 (2)
C(48)	0.0882 (3)	−0.0005 (6)	1.0491 (3)	0.070 (2)
C(49)	0.0891 (3)	−0.0890 (5)	1.0210 (4)	0.074 (2)
C(50)	0.1348 (3)	−0.1096 (4)	0.9770 (3)	0.061 (2)

Cl(1)	0.0210 (2)	0.2650 (2)	0.6341 (2)	0.167 (1)
Cl(2)	0.0491 (2)	0.0716 (3)	0.6059 (2)	0.226 (2)
C(51)	0.0790 (5)	0.1722 (7)	0.6512 (5)	0.132 (4)

Table 2. *Geometric parameters* (Å, °)

Ir(1)—Ir(2)	3.307 (1)	N(3)—N(4)	1.376 (6)
Ir(1)—N(1)	2.075 (4)	N(3)—C(8)	1.337 (7)
Ir(1)—N(3)	2.091 (4)	N(4)—C(9)	1.332 (7)
Ir(2)—N(2)	2.068 (4)	O(1)—C(1)	1.174 (7)
Ir(2)—N(4)	2.073 (4)	O(2)—C(2)	1.165 (7)
Ir(1)—C(1)	1.797 (6)	C(3)—C(5)	1.371 (8)
Ir(2)—C(2)	1.810 (6)	C(3)—C(6)	1.493 (9)
Ir(1)—P(1)	2.224 (1)	C(4)—C(5)	1.377 (8)
Ir(2)—P(2)	2.224 (1)	C(4)—C(7)	1.494 (8)
P(1)—O(3)	1.629 (4)	C(8)—C(10)	1.365 (9)
P(2)—O(4)	1.633 (4)	C(8)—C(11)	1.488 (9)
N(1)—N(2)	1.370 (6)	C(9)—C(10)	1.377 (9)
N(1)—C(3)	1.349 (7)	C(9)—C(12)	1.493 (9)
N(2)—C(4)	1.334 (7)		
P(1)—Ir(1)—N(3)	92.3 (1)	Ir(2)—P(2)—C(39)	117.8 (2)
P(1)—Ir(1)—C(1)	91.0 (2)	Ir(1)—N(1)—N(2)	117.9 (3)
N(1)—Ir(1)—N(3)	85.1 (2)	Ir(1)—N(1)—C(3)	135.1 (3)
N(1)—Ir(1)—C(1)	91.6 (2)	C(3)—N(1)—N(2)	106.8 (4)
P(1)—Ir(1)—N(1)	177.4 (1)	Ir(2)—N(2)—N(1)	117.1 (3)
N(3)—Ir(1)—C(1)	176.3 (2)	Ir(2)—N(2)—C(4)	133.0 (3)
P(2)—Ir(2)—N(2)	92.5 (1)	C(4)—N(2)—N(1)	109.3 (4)
P(2)—Ir(2)—C(2)	91.8 (2)	Ir(1)—N(3)—N(4)	117.2 (3)
N(2)—Ir(2)—N(4)	83.1 (2)	Ir(1)—N(3)—C(8)	134.3 (4)
P(2)—Ir(2)—N(4)	174.2 (1)	C(8)—N(3)—N(4)	108.4 (4)
N(2)—Ir(2)—C(2)	174.1 (2)	C(9)—N(4)—N(3)	107.4 (4)
N(4)—Ir(2)—C(2)	92.9 (2)	Ir(2)—N(4)—N(3)	118.0 (3)
Ir(1)—C(1)—O(1)	179.3 (5)	Ir(2)—N(4)—C(9)	134.5 (4)
Ir(2)—C(2)—O(2)	178.0 (5)	C(5)—C(3)—N(1)	109.2 (5)
Ir(1)—P(1)—O(3)	119.3 (1)	C(5)—C(4)—N(2)	108.2 (5)
Ir(1)—P(1)—C(27)	116.5 (2)	C(4)—C(5)—C(3)	106.5 (5)
Ir(1)—P(1)—C(45)	116.4 (2)	C(10)—C(8)—N(3)	108.6 (5)
Ir(2)—P(2)—O(4)	119.7 (1)	C(10)—C(9)—N(4)	109.1 (5)
Ir(2)—P(2)—C(33)	116.2 (2)	C(9)—C(10)—C(8)	106.5 (5)

Weights were taken as $1/\sigma^2(F_o^2)$; variances $[\sigma^2(F_o^2)]$ derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014\langle I\rangle)^2$. Goodness of fit for merging data was 1.02; R_{merge} for duplicates, 0.020. Dispersion corrections were taken from Cromer & Waber (1974). The final R for $F_o^2 > 3\sigma$ was 0.0235; the final wR, 0.0022. Since the calculated absorption correction increased the goodness of fit for merging, an absorption coefficient corresponding to 30% of the calculated value was used.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55976 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1021]

References

Beveridge, K. A, Bushnell, G. W., Dixon, K. R., Eadie, D. T., Stobart, S. R., Atwood, J. L. & Zaworotko, M. J. (1982). *J. Am. Chem. Soc.* **104**, 920-921.

Beveridge, K. A., Bushnell, G. W. & Stobart, S. R. (1983). *Organometallics*, **2**, 1447-1451.

Coleman, A. W., Eadie, D. T., Stobart, S. R., Zaworotko, M. J. & Atwood, J. L. (1982). *J. Am. Chem. Soc.* **104**, 922-923.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 99-101. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Duchamp, D. J. (1964). Am. Crystallogr. Assoc. Meet., Bozeman, Montana. Abstract B14, pp. 29-30.

Farid, R. S., Chang, I.-J., Winkler, J. R. & Gray, H. B. (1993). In preparation.

Fox, L. S. (1989). PhD dissertation, California Institute of Technology, USA.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Louie, B. M., Rettig, S. J., Storr, A. & Trotter, J. (1984). *Can. J. Chem.* **62**, 1057-1067.

Nussbaum, S., Rettig, S. J., Storr, A. & Trotter, J. (1985). *Can. J. Chem.* **63**, 692-702.

Schagen, J. D., Straver, L., van Meurs, F. & Williams, G. (1989). CAD-4 manual. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Uson, R., Oro, L. A., Ciriano, M. A., Pinillos, M. T., Tiripicchio, A. & Carmellini, M. (1981). *J. Organomet. Chem.* **205**, 247-257.

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Structure of [*N*,*N*′-*o*-Phenylenebis(salicylideneaminato)]iron(III) Chloride as a Five-Coordinate Monomer

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Abstract

The crystal contains three independent five-coordinate monomers of chloro{2,2′-[*o*-phenylenebis(nitrilomethylidyne)]diphenolato-*N*,*N*′,*O*,*O*′}iron(III). The distances Fe(1)—Fe(1*A*), Fe(1)—Fe(1*B*) and Fe(1*A*)—Fe(1*B*) are 7.175 (1), 7.683 (1) and 7.207 (1) Å, respectively. The planes of the ligand groups of the two neighbouring molecules bend away from each other.

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