

Crystal Structure and Catalytic Properties of a Platinum–Iridium Mixed Cluster, $[\text{Pt}_2\text{Ir}_2(\mu\text{-CO})_3(\text{CO})_4(\text{PPh}_3)_3]^\dagger$

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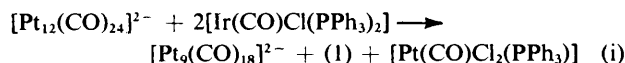
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The compound $[\text{Pt}_2\text{Ir}_2(\text{CO})_7(\text{PPh}_3)_3]$ has been synthesised from $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ and $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$. A single-crystal X-ray structure determination (space group $P\bar{1}$, $Z = 2$, $R = 0.050$ for 5 402 reflections) has shown that the metal atoms adopt a 'butterfly' configuration with the iridium and platinum atoms occupying 'hinge' and 'wing-tip' positions respectively. The mixed-metal cluster is an active catalyst for hydrogenation of olefins.

Mixed-metal carbonyl clusters are of interest as precursors for the preparation of alloy-type heterogeneous catalysts and also as homogeneous catalysts of high activity.¹⁻³ Despite the rapid growth in the number of mixed-metal clusters reported, there appears to be no previous crystallographic study of an iridium–platinum cluster; structures have been reported for two hydrido-bridged binuclear IrPt complexes.^{4,5} Here we report the synthesis and crystal structure determination of $[\text{Pt}_2\text{Ir}_2(\text{CO})_7(\text{PPh}_3)_3]$ (1), which is also found to catalyse olefin-hydrogenation reactions.

Results and Discussion

Synthesis and Studies on Catalytic Reactions.—Reaction of $[\text{NBu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ (2) with $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ under ambient conditions leads to the formation of (1) according to reaction (i). Since both $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ and (2) have characteris-



tic bands in the visible region, the course of the reaction and formation of $[\text{Pt}_9(\text{CO})_{18}]^{2-}$ are conveniently monitored by spectrophotometry.⁶ Attempts to synthesise the rhodium analogue of complex (1) from the reaction of (2) with $[\text{Rh}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ have been unsuccessful. Reactions of (2) with other iridium complexes such as $[\text{Ir}(\text{NO})(\text{CO})(\text{PPh}_3)_2]$, $[\text{Ir}(\text{NO})(\text{CO})\text{Cl}(\text{PPh}_3)_2]^+$, $[\{\text{Ir}(\text{cod})\text{Cl}\}_2]$ (cod = cyclo-octa-1,5-diene), and $[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ have so far not yielded any isolable Pt–Ir mixed cluster.

No reaction is observed between complex (1) and hydrogen under relatively mild conditions ($\leq 20 \text{ lbf in}^{-2}$, $\leq 60^\circ\text{C}$, 5 h), as judged by solution i.r. spectroscopy. Under high pressures of hydrogen ($\geq 150 \text{ lbf in}^{-2}$) a red-brown, as yet uncharacterised carbonyl complex could be isolated. One of the general

[†] 1,2;1,3;2,3-Tri- μ -carbonyl-2,2,3-tricarbonyl-2,3- μ -[carbonyl(tri-phenylphosphine)platinio]-1,3-bis(tri-phenylphosphine)platinum-iridium (4 Pt–Ir, 1 Ir–Ir).

Supplementary data available (No. SUP 56049, 6 pp.): H-atom coordinates, thermal parameters, other bond lengths, full bond angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Non-S.I. units employed: $\text{lbf in}^{-2} \approx 6.89 \times 10^3 \text{ Pa}$, $\text{mmHg} \approx 133 \text{ Pa}$.

Table 1. Catalytic activity of complex (1)

Reactant	Product	Turnover number ^a (h ⁻¹)
Cyclohexene ^b	Cyclohexane	320
2-Methylcyclohexene ^b	2-Methylcyclohexane	290
Cyclohexen-2-one ^c	Cyclohexanone ^d	63
Crotonaldehyde ^c	Butyraldehyde ^e	26
Cyclohexene ^f	Cyclohexane + benzene	0.5

^a (Moles of product)/(moles of catalyst \times time). ^b Reaction conditions: p_{H_2} (initial) = 10 lbf in^{-2} , 70°C , 0.005 mmol (1), 25 mmol reactant, no solvent, 5 h. ^c Conditions as in footnote b but with cyclohexane solvent. ^d Trace amounts of cyclohexanol. ^e Trace amounts of BuⁿOH and but-2-enyl alcohol. ^f Conditions as in footnote b but under vacuum in a sealed tube (10^{-3} mmHg) at 100°C .

methods of anionic carbonyl-cluster synthesis by reaction of neutral clusters with base⁷ fails with (1), as the cluster is found to be inert towards concentrated methanolic KOH or alkoxides.

Since Pt–Ir alloy systems have recently been investigated as reformation catalysts,⁸ complex (1) has been tested as a catalyst for H–D exchange between $[\text{H}_4]$ methanol and cyclohexane. No exchange has been observed in this reaction, but (1) shows low catalytic activity for cyclohexene disproportionation to cyclohexane and benzene (see Table 1). The reaction mixture remains homogeneous throughout the course of this reaction, as demonstrated by the lack of light scattering. The characteristic i.r. and u.v.–visible spectra of complex (1) (see Experimental section) allow solution spectroscopic investigations of this catalytic reaction. Such studies do not indicate formation of any other complex than (1) at any stage of the reaction.

Considerable catalytic activity is observed when complex (1) is used as a catalyst for the hydrogenation of cyclohexene, 2-methylcyclohexene, crotonaldehyde (but-2-enol), and cyclohexen-2-one (see Table 1). For the last two compounds only the olefinic linkages are hydrogenated, the carbonyl groups remaining unchanged. The homogeneous nature of the reaction mixture has been demonstrated by the absence of light scattering and by carrying out filtration through a micro-pore filter to establish that the catalytic activities remain unchanged after filtration. Here again solution spectrophoto-

Table 2. Atomic co-ordinates ($\times 10^4$) *

Atom	x	y	z	Atom	x	y	z
Pt(1)	2 811(1)	1 426(1)	1 791(1)	C(233)	-2 268	3 401	2 854
Pt(2)	1 908(1)	2 637(1)	3 049(1)	C(234)	-1 780	4 359	3 143
Ir(3)	2 937(1)	3 242(1)	1 728(1)	C(235)	-699	4 655	3 544
Ir(4)	4 069(1)	2 740(1)	3 077(1)	C(236)	-106	3 992	3 656
P(1)	3 144(3)	15(3)	2 018(2)	C(231)	-594	3 034	3 367
C(112)	2 567(7)	31(7)	3 666(6)	P(3)	3 341(3)	4 888(3)	1 935(3)
C(113)	2 603	-175	4 506	C(312)	2 872(7)	5 185(6)	3 652(7)
C(114)	3 360	-641	4 802	C(313)	2 624	5 712	4 379
C(115)	4 082	-899	4 258	C(314)	2 336	6 551	4 310
C(116)	4 046	-692	3 418	C(315)	2 295	6 864	3 514
C(111)	3 289	-228	3 122	C(316)	2 543	6 337	2 787
C(122)	5 146(8)	572(6)	1 419(6)	C(311)	2 831	5 498	2 855
C(123)	6 052	431	1 036	C(322)	1 783(8)	4 890(6)	548(7)
C(124)	6 153	-482	786	C(323)	1 375	5 214	-173
C(125)	5 348	-1 255	918	C(324)	2 006	5 995	-454
C(126)	4 442	-1 113	1 301	C(325)	3 045	6 453	-13
C(121)	4 341	-200	1 551	C(326)	3 453	6 129	708
C(132)	1 863(9)	-1 110(7)	544(7)	C(321)	2 822	5 347	989
C(133)	1 035	-1 862	75	C(332)	5 302(10)	6 167(8)	2 795(7)
C(134)	410	-2 512	509	C(333)	6 411	6 608	2 847
C(135)	613	-2 409	1 411	C(334)	7 005	6 344	2 196
C(136)	1 441	-1 657	1 880	C(335)	6 489	5 639	1 492
C(131)	2 066	-1 008	1 446	C(336)	5 380	5 198	1 439
P(2)	261(3)	2 228(3)	3 522(2)	C(331)	4 786	5 462	2 091
C(212)	568(9)	1 331(7)	4 908(6)	C(1)	4 519(13)	3 043(12)	1 857(11)
C(213)	651	1 224	5 778	O(1)	5 274(8)	3 057(8)	1 485(7)
C(214)	467	1 913	6 408	C(2)	5 014(10)	2 032(9)	3 389(9)
C(215)	199	2 708	6 168	O(2)	5 606(8)	1 576(8)	3 596(8)
C(216)	116	2 815	5 298	C(3)	2 705(12)	3 073(10)	509(10)
C(211)	300	2 127	4 668	O(3)	2 595(11)	2 905(9)	-218(6)
C(222)	-200(7)	566(9)	2 342(7)	C(4)	2 923(11)	2 396(11)	4 045(10)
C(223)	-823	-327	1 935	O(4)	3 001(9)	2 277(9)	4 751(6)
C(224)	-1 827	-715	2 196	C(5)	1 316(12)	3 118(11)	1 974(8)
C(225)	-2 207	-210	2 865	O(5)	493(8)	3 220(8)	1 643(7)
C(226)	-1 584	683	3 273	C(6)	1 753(13)	1 007(10)	785(10)
C(221)	-580	1 071	3 011	O(6)	1 110(10)	781(9)	204(8)
C(232)	-1 675(9)	2 738(7)	2 966(7)	C(7)	4 903(12)	3 902(12)	3 756(9)
				O(7)	5 453(10)	4 587(8)	4 168(7)

* Atoms without e.s.d.s. are in rigid groups, for which common e.s.d.s. are given and are omitted from all but the first atom of each group.

metric and i.r. studies do not indicate formation of any other carbonyl complex to a detectable extent.

It should be pointed out that work in the area of cluster catalysis with framework asymmetric clusters has recently been reported.⁹ The inherent asymmetry of complex (1) (see later), its reasonably high-yield synthesis, and the fact that it is an active catalyst for olefin-hydrogenation reactions make it a potential candidate for such work. Successful resolution of (1), however, is necessary before catalytic asymmetric hydrogenation of prochiral olefins can be attempted with this cluster. Unfortunately, the method reported by Brunner,¹⁰ based on the formation of diastereomers through the attack of methoxide ion on the carbonyl ligand, is not applicable in this case because of the absence of reactivity of (1) towards alkoxides.

Crystal Structure of Complex (1).—Although atomic absorption spectroscopy indicated the presence of Pt and Ir in an equimolar ratio, the exact geometry of the metal framework and the disposition of the carbonyl groups could be ascertained only by single-crystal X-ray diffraction studies. The four metal atoms adopt a butterfly configuration (Figure) with the non-bonded Pt(1) \cdots Pt(2) distance being 2.976(1) Å. This value is close to the non-bonded Pt \cdots Pt distance of 2.987(4) Å observed¹¹ in $[\text{Co}_2\text{Pt}_2(\text{CO})_8(\text{PPh}_3)_2]$ (3). The Ir–Ir and average Pt–Ir bond distances are 2.741(1) and 2.693(1) Å respectively. The Ir–Ir distance is longer than that observed

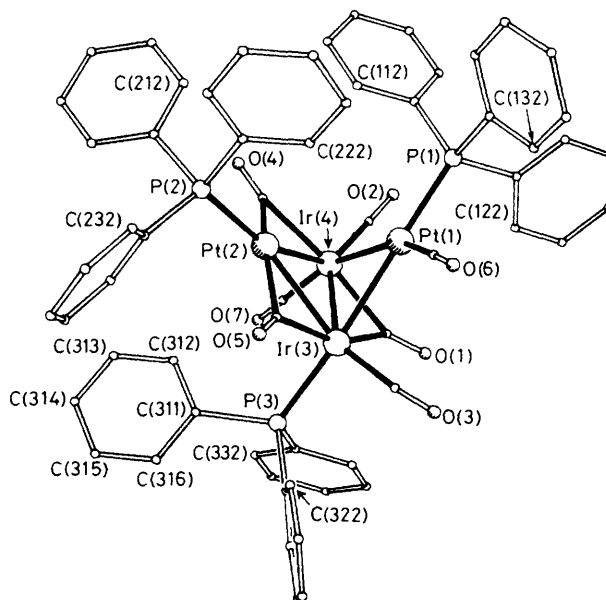


Figure. Molecular structure of complex (1), showing the atom labelling scheme. Only one phenyl ring is labelled in full; the same scheme is used for the others, for which only one *ortho*-carbon atom is labelled. Carbonyl C atoms bear the same numbers as the O atoms

Table 3. Selected bond lengths (Å)

Pt(1)···Pt(2)	2.976(1)	Pt(1)–Ir(3)	2.675(1)
Pt(1)–Ir(4)	2.681(1)	Pt(2)–Ir(3)	2.704(1)
Pt(2)–Ir(4)	2.714(1)	Ir(3)–Ir(4)	2.741(1)
Pt(1)–P(1)	2.300(4)	Pt(2)–P(2)	2.264(4)
Ir(3)–P(3)	2.336(4)	Pt(1)–C(6)	1.898(15)
Pt(2)–C(4)	2.058(15)	Pt(2)–C(5)	2.070(15)
Ir(3)–C(1)	2.100(18)	Ir(3)–C(3)	1.880(15)
Ir(3)–C(5)	2.105(15)	Ir(4)–C(1)	2.129(18)
Ir(4)–C(2)	1.852(15)	Ir(4)–C(4)	2.233(15)
Ir(4)–C(7)	1.899(14)		

in $[\text{Ir}_4(\text{CO})_{12}]$ (2.693 Å) but comparable to the mean distance of 2.73 Å observed¹² in $[\text{Ir}_4(\text{CO})_6(\text{PPh}_3)_3]$. The two PtIr_2 triangles subtend an angle of 79.8(1)°.

The ligands are distributed among the metal centres in the following way: one PPh_3 ligand is associated with each platinum and Ir(3), while Pt(1) and Ir(3) also have one terminal carbonyl group each; Ir(4) has two terminal carbonyl groups. The remaining three carbonyl groups bridge Ir(3)–Ir(4), Pt(2)–Ir(3), and Pt(2)–Ir(4) bonds. The observed structure is therefore similar to that of complex (3), except that one iridium atom in (1) is bonded to a phosphine, whereas phosphine substitution does not involve the cobalt atoms in (3).

It is interesting to note that in all the crystallographically characterised metal clusters containing two platinum atoms, (1), (3), and $[\text{Os}_2\text{Pt}_2\text{H}_2(\text{CO})_8(\text{PPh}_3)_2]$,¹³ the metals define a 'butterfly' configuration with no bonding interaction between the platinum atoms. The 16-electron configurations of the platinum atoms in these complexes have recently been rationalised¹⁴ on the basis of the expected frontier molecular orbitals of 'Pt(PH₃)₂' fragments.

Experimental

Infrared spectra were taken on a Perkin-Elmer 377 grating spectrometer. A Carlo-Erba 1106 instrument was used for microanalyses. Metal estimation and gas chromatographic analyses were performed on IL 751 atomic absorption spectrophotometer and Pye-Unicam 204 instrument respectively. U.v.–visible spectra were recorded on a Pye-Unicam SP8 100 spectrometer. The salt $[\text{NBu}^n_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ was prepared and catalytic experiments were carried out according to previously reported procedures.¹⁵

Synthesis of Complex (1).—The complex $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ (0.100 g, 0.128 mmol) in degassed chloroform (30 cm³) was added to a solution of $[\text{NBu}^n_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ (0.175 g, 0.05 mmol) in degassed acetonitrile (50 cm³). The solution was stirred at ambient temperature and a gentle stream of nitrogen was bubbled through it. After 3 h the colour had changed from blue-green to red-brown. The solvent was removed under pressure. The residue was subjected to thin-layer chromatography with n-hexane–chloroform (70 : 30) as eluant. A yellow band was isolated and the product (1) recrystallised from cyclohexane, yield 0.057 g (0.065 mmol) {Found: C, 42.1; H, 2.7. Calc. for $[\text{Pt}_2\text{Ir}_2(\text{CO})_7(\text{PPh}_3)_3]$: C, 41.7; H, 2.6%. Infrared spectrum (cyclohexane): 2 040s, 2 020vs, 1 985 (sh), 1 980s, 1 860w, 1 815s, and 1 790s cm⁻¹. U.v.–visible: λ_{max} at 340 nm ($\epsilon = 5\,000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$).

Crystallography.—Crystal data. $\text{C}_{61}\text{H}_{45}\text{Ir}_2\text{O}_7\text{P}_3\text{Pt}_2$, $M = 1\,757.6$, triclinic, $a = 12.728(2)$, $b = 14.824(2)$, $c = 15.704(4)$

Å, $\alpha = 98.23(1)$, $\beta = 95.49(1)$, $\gamma = 103.93(1)^\circ$, $U = 2\,820\text{ Å}^3$, (by least-squares refinement of 2θ angles for 40 reflections, $\lambda = 0.710\,69\text{ Å}$), space group $P\bar{1}$, $Z = 2$, $D_c = 2.07\text{ g cm}^{-3}$, $F(000) = 1\,644$, crystal dimensions $0.12 \times 0.2 \times 0.2\text{ mm}$, $\mu(\text{Mo-K}\alpha) = 98.2\text{ cm}^{-1}$.

Data collection and processing. Stoe-Siemens AED diffractometer, ω – θ scan mode, graphite-monochromated Mo-K α radiation, on-line profile fitting.¹⁶ 7 514 Reflections measured ($2\theta < 45^\circ$, $h \leq 0$), of which 7 351 unique (merging $R = 0.025$), giving 5 402 with $F > 4\sigma(F)$; no significant intensity variation for three standard reflections. Empirical absorption corrections based on azimuthal scan data¹⁷ (minimum and maximum transmission factors = 0.139 and 0.236).

Structure solution and refinement.¹⁷ Patterson synthesis (Ir and Pt), difference syntheses. Blocked-cascade refinement on F , with all non-hydrogen atoms anisotropic, rigid ideal hexagons for phenyl groups (C–C 1.395 Å), hydrogens in calculated positions with $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,06\,F^2$, giving satisfactory analysis of variance. Final $R = 0.050$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2} = 0.040$. Slope of normal probability plot = 1.44; largest peaks in final difference synthesis ca. 1.2 e Å^{-3} , all close to metal atoms. Scattering factors from ref. 18. Refined co-ordinates are given in Table 2, selected bond lengths in Table 3.

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