Homo- and Hetero-dinuclear Hydride-bridged Complexes containing Cyclo-octadiene: the Crystal and Molecular Structure of $[(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-}H)(\mu\text{-}Cl)\text{-}IrH_2(PPh_3)_2]$†

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The reaction of $[IrH_5(PPh_3)_2]$ with $[\{M(cod)Cl\}_2]$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene) gives the dinuclear complexes $[(\eta^4\text{-}C_8H_{12})M(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2]$. The di-iridium compound has been subjected to an *X*-ray analysis which establishes that the iridium(I) atom adopts a square-planar co-ordination geometry while the iridium(III) atom is in a pseudo-octahedral environment if the direct Ir–Ir interaction is ignored. The two Ir atoms are bridged by a hydride and a chloride ligand. The Ir–Cl bridge is highly asymmetric [Ir(1)–Cl(1) 2.352(8), Ir(2)–Cl(1) 2.534(8) Å], and this asymmetry is discussed in terms of the relative *trans* effect of the ligands present.

The 'donor–acceptor' route [equation (1)] has opened the way

$$\underset{\text{acceptor}}{L_mM} + \underset{\text{donor}}{H\text{-}M'L'_n} \longrightarrow \underset{\text{bridged complex}}{L_mM\text{-}H\text{-}M'L'_n} \qquad (1)$$

for the directed preparation of many hydride-bridged metal complexes.[1,2] Organometallic compounds containing cyclo-octadiene ligands have not yet been represented among these, though complexes containing cyclopentadienyl, pentamethyl-cyclopentadienyl, and alkyl groups are known.[1]

Results and Discussion

When stoicheiometric amounts of $[IrH_5(PPh_3)_2]$ and $[\{M(cod)(\mu\text{-}Cl)\}_2]$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene) react in tetrahydrofuran (thf) the mixed-valence dimers (**1**) and (**2**) are formed as pale yellow, air-stable complexes [equation (2)].

$$[\{M(cod)(\mu\text{-}Cl)\}_2] \xrightarrow[\text{thf}]{[IrH_5(PPh_3)_2]} [(cod)M(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2] \qquad (2)$$

(**1**) M = Rh
(**2**) M = Ir

Similar cleavage of $(\mu\text{-}Cl)_2$ bridges by iridium pentahydrides has been used in preparing $[(R_3P)_2M(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PR_3)_2]$.[3]

A crystal of complex (**2**) has been studied by *X*-ray diffraction and the structure is illustrated in the Figure. Selected bond parameters are presented in Table 1. One iridium atom, Ir(1), adopts a distorted square-planar geometry *via* co-ordination to cyclo-octadiene and the bridging halide and hydride. The second iridium atom, Ir(2), displays a distorted octahedral geometry with the phosphines occupying *trans* axial sites. The hydrides were not located directly, but their positions were obtained by potential-energy calculations,[4] and were not included in the refinement cycles. The Ir(1)–Ir(2) distance may indicate the presence of a direct metal–metal interaction within the molecule. It is similar in length to the Rh–Ir bond [2.899(1) Å] in $[(Et_3P)_2Rh(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PEt_3)_2]$,[3] but in both systems the presence of bridging ligands prevents an analysis of the extent of the metal–metal interaction.

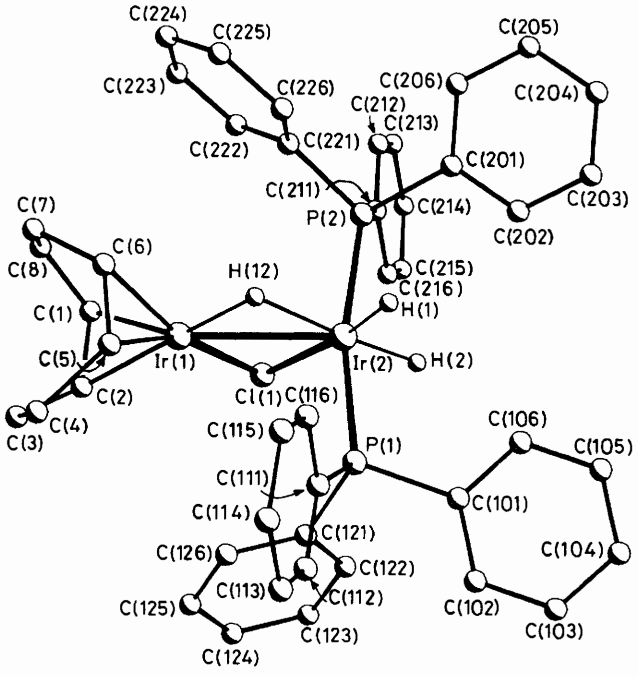

Figure. Molecular structure of $[(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-}H)(\mu\text{-}Cl)\text{-}IrH_2(PPH_3)_2]$ (**2**). Phenyl and C_8H_{12} hydrogen atoms have been omitted for clarity

The considerable *trans* influence of the hydride ligand is reflected in the greatly disparate Ir–Cl distances, with Ir(1)–Cl(1) [Cl *trans* to C(5)–C(6)] being *ca.* 0.18 Å shorter than Ir(2)–Cl(1) [Cl *trans* to H(1)]. This gross asymmetry in the $Ir_2(\mu\text{-}Cl)$ bridge can be compared with the situation in $[(Et_3P)_2Rh(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PEt_3)_2]$, where the Rh–Cl distance is 2.427(3) Å (Cl *trans* to PEt_3) and the Ir–Cl distance is 2.494(3) Å (Cl *trans* to H).[3] While the *trans* influence of PEt_3 is less than that of H^-, it is greater than that of an olefin[5,6] and might be expected to level the difference in M–Cl distances somewhat. The asymmetry in complex (**2**) is striking though for its magnitude. Another comparison in bridging systems can be made with *cis*-$[\{Ir(CO)Me(\mu\text{-}Cl)Cl\}_2]$[7] which exhibits Ir–Cl (bridge) distances of 2.38 Å (Cl *trans* to CO) and 2.52 Å (Cl *trans* to Me). Further

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† μ-Chloro-2-η-cyclo-octa-1,5-diene-μ-hydrido-1,1-dihydrido-1,1-bis-(triphenylphosphine)di-iridium(III,I).

Supplementary data available (No. SUP 56209, 7 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

studies on the structural *trans* influence of ligands in mixed-valence dimers like (**1**) and (**2**) would be profitable.

The axial phosphines on Ir(2) are bent away from Ir(1), and the phenyl rings on each group are staggered with respect to each other. The other parameters within the phosphines do not deviate from the expected values.

The hydride region of the ^1H n.m.r. spectra of complexes (**1**) and (**2**) (Table 2) shows the terminal hydrides H(1) and H(2) appearing as triplets of doublets of doublets at δ -22 and -11, respectively. Their assignments are based on the relative magnitudes of the coupling constant to that of the bridging hydride H(12): the *trans* hydride should have the larger coupling to H(12). The bridging hydride H(12) appears as an apparent triplet with unresolved coupling to the terminal hydrides. In complexes (**1**) and (**2**) the coupling constant ^2J[PH(12)] is less than ^2J(PH) for the terminal hydrides (6.6—8.0 *vs.* 16.4—17.5 Hz). This phenomenon is probably due to a reduced bond order in μ-H systems.[8]

Table 1. Selected bond lengths (Å) and angles (°) for $[(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2]$

Ir(1)–Ir(2)	2.827(2)	Ir(2)–Cl(1)	2.534(8)
Ir(1)–Cl(1)	2.352(8)	Ir(2)–P(1)	2.291(7)
Ir(1)–C(1)	2.17(3)	Ir(2)–P(2)	2.301(7)
Ir(1)–C(2)	2.13(3)	P(1)–C(101)	1.82(2)
Ir(1)–C(5)	2.08(4)	P(1)–C(111)	1.85(2)
Ir(1)–C(6)	2.15(4)	P(1)–C(121)	1.80(2)
C(1)–C(2)	1.43(5)	P(2)–C(201)	1.83(2)
C(2)–C(3)	1.52(6)	P(2)–C(211)	1.85(2)
C(3)–C(4)	1.48(5)	P(2)–C(221)	1.79(2)
C(4)–C(5)	1.66(6)	C(6)–C(7)	1.54(5)
C(5)–C(6)	1.41(6)	C(7)–C(8)	1.52(6)
C(8)–C(1)	1.50(6)		
Ir(2)–Ir(1)–Cl(1)	57.7(2)	Ir(1)–Ir(2)–P(1)	96.3(2)
Ir(1)–Ir(2)–Cl(1)	51.7(2)	Ir(1)–Ir(2)–P(2)	96.5(2)
Ir(1)–Cl(1)–Ir(2)	70.6(2)	Cl(1)–Ir(2)–P(1)	96.4(3)
Ir(2)–Ir(1)–C(1)	143.4(9)	Cl(1)–Ir(2)–P(2)	93.8(3)
Ir(2)–Ir(1)–C(2)	147.5(11)	P(1)–Ir(2)–P(2)	166.9(2)
Ir(2)–Ir(1)–C(5)	114.7(12)	Ir(2)–P(1)–C(101)	114.9(16)
Ir(2)–Ir(1)–C(6)	119.4(10)	Ir(2)–P(1)–C(111)	118.6(6)
Cl(2)–Ir(1)–C(1)	92.5(9)	Ir(2)–P(1)–C(121)	114.5(7)
Cl(1)–Ir(1)–C(2)	93.7(10)	Ir(2)–P(2)–C(201)	114.1(6)
Cl(1)–Ir(1)–C(5)	157.3(11)	Ir(2)–P(2)–C(211)	116.3(7)
Cl(1)–Ir(1)–C(6)	163.3(11)	Ir(2)–P(2)–C(221)	117.2(7)

The reaction of $[IrH_5(PPh_3)_2]$ with $[\{Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2]$ and $[\{Rh(CO)_2(\mu\text{-}Cl)\}_2]$ resulted in rapid decomposition to uncharacterised black products. However, work on the preparation of other hydride-bridged dimers using different donors and acceptors is continuing.

Compound (**2**) does not react with H_2 (1 atm, 101 325 Pa), but reaction with PPh_3 (2:1 equivalent excess, refluxing thf) results in a cleavage of the bridge and formation of several products, among which could be identified (by ^1H n.m.r.) $[IrH_3(PPh_3)_3]$, $[IrH_2Cl(PPh_3)_3]$, and $[Ir(cod)Cl(PPh_3)_2]$.

Experimental

Although neither complex (**1**) nor (**2**) was air sensitive, reactions were carried out under N_2. The complexes $[\{Rh(cod)Cl\}_2]$,[9] $[\{Ir(cod)Cl\}_2]$,[10] and $[IrH_5(PPh_3)_2]$[11] were prepared by literature methods. Tetrahydrofuran was dried over and distilled from sodium–benzophenone.

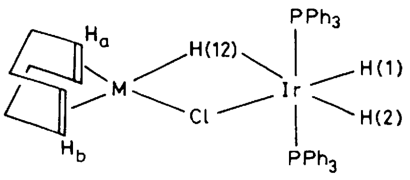
Preparations.—$[(\eta^4\text{-}C_8H_{12})Rh(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2]$ (**1**). The complex $[\{Rh(cod)Cl\}_2]$ (20 mg, 0.04 mmol) and $[IrH_5(PPh_3)_2]$ (60 mg, 0.083 mmol) were heated in thf (10 cm^3) until the suspension cleared (reflux for *ca.* 5 min). The clear yellow solution was cooled, the solvent removed *in vacuo*, and the residue purified by column chromatography (alumina, toluene eluant) to give a single mobile yellow band. This was crystallised from Et_2O–heptane; yield 46 mg (58%) (Found: C, 54.55; H, 4.75. Calc. for $C_{44}H_{45}ClIrP_2Rh$: C, 54.80; H, 4.70%).

$[(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2]$ (**2**). This was prepared in a similar manner to (**1**) using $[\{Ir(cod)Cl\}_2]$ (28 mg, 0.041 mmol) and $[IrH_5(PPh_3)_2]$ (60 mg, 0.083 mmol). Yield 39 mg (44%) (Found: C, 50.10; H, 4.35. Calc. for $C_{44}H_{45}ClIr_2P_2$: C, 50.25; H, 4.30%).

Crystal Structure Determination of $[(\eta^4\text{-}C_8H_{12})Ir(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2]$.—Suitable single crystals were obtained as yellow-orange blocks by slow evaporation of a CH_2Cl_2–heptane solution, and a crystal with dimensions *ca.* 0.334 × 0.395 × 0.494 mm was sealed in a 0.5-mm glass capillary.

Crystal data. $C_{44}H_{45}ClIr_2P_2$, M = 1 055.59, monoclinic, a = 16.644(10), b = 12.631(10), c = 18.302(14) Å, β = 93.23(6)°, U = 3 841.5 Å^3 (by least-squares refinement for 50 automatically centred reflections in the range $15 < 2\theta < 25°$), space group $P2_1/c$ (no. 14), D_m not measured, Z = 4, D_c = 1.825 g cm^{-3},

Table 2. Proton n.m.r. data for compounds (**1**) and (**2**)[a]



Compound	H_a	H_b	H(1)	H(2)	H(12)[b]
(**1**)	4.18	4.52	-21.84 ^2J[PH(1)] = 16.6(t) ^2J[H(1)H(2)] = 6.1(d) ^2J[H(1)H(12)] = 1.8(d)	-11.13 ^2J[PH(2)] = 17.3(t) ^2J[H(2)H(1)] = 6.1(d) ^2J[H(2)H(12)] = 3.4(d)	-14.17 ^2J[PH(12)] = 8.0(t) ^1J[RhH(12)] = 24.4(d)
(**2**)	3.92	4.22	-22.47 ^2J[PH(1)] = 16.4(t) ^2J[H(1)H(2)] = 6.1(d) ^2J[H(1)H(12)] = 1.6(d)	-11.36 ^2J[PH(2)] = 17.5(t) ^2J[H(2)H(1)] = 6.1(d) ^2J[H(2)H(12)] = 2.6(d)	-9.1 ^2J[PH(12)] = 6.6(t)

[a] In C_6D_6 solution; δ in p.p.m., J in Hz; t = triplet and d = doublet. [b] Coupling to H(1) and H(2) not resolved.

Table 3. Atomic fractional co-ordinates (× 10^4) for [(η^4-C_8H_{12})Ir(μ-H)(μ-Cl)IrH_2(PPh_3)$_2$]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ir(1)	1 662(1)	5 273(1)	2 574(1)	C(203)	5 077(10)	2 051(14)	4 284(8)
Ir(2)	2 732(1)	4 439(1)	3 682(1)	C(204)	5 506(10)	1 458(14)	3 793(8)
Cl(1)	1 226(5)	4 162(6)	3 504(4)	C(205)	5 199(10)	1 321(14)	3 075(8)
P(1)	2 672(4)	5 851(5)	4 463(4)	C(206)	4 464(10)	1 776(14)	2 846(8)
C(101)	3 234(9)	5 683(13)	5 339(10)	C(211)	2 412(11)	1 743(15)	3 248(9)
C(102)	3 037(9)	6 271(13)	5 949(10)	C(212)	2 495(11)	814(15)	2 847(9)
C(103)	3 506(9)	6 186(13)	6 602(10)	C(213)	2 057(11)	−86(15)	3 016(9)
C(104)	4 172(9)	5 514(13)	6 646(10)	C(214)	1 537(11)	−58(15)	3 587(9)
C(105)	4 369(9)	4 926(13)	6 036(10)	C(215)	1 454(11)	871(15)	3 989(9)
C(106)	3 900(9)	5 011(13)	5 382(10)	C(216)	1 891(11)	1 771(15)	3 819(9)
C(111)	3 128(10)	7 121(14)	3 660(9)	C(221)	3 041(9)	2 978(14)	2 095(10)
C(112)	2 963(10)	8 061(14)	4 561(9)	C(222)	2 412(9)	2 582(14)	1 638(10)
C(113)	3 358(10)	8 993(14)	4 385(9)	C(223)	2 422(9)	2 717(14)	883(10)
C(114)	3 918(10)	8 984(14)	3 846(9)	C(224)	3 062(9)	3 248(14)	584(10)
C(115)	4 083(10)	8 044(14)	3 483(9)	C(225)	3 690(9)	3 644(14)	1 041(10)
C(116)	3 688(10)	7 112(14)	3 660(9)	C(226)	3 680(9)	3 509(14)	1 797(10)
C(121)	1 668(12)	6 218(15)	4 686(10)	C(1)	626(18)	4 892(27)	1 848(18)
C(122)	1 313(12)	5 723(15)	5 268(10)	C(2)	480(18)	5 820(26)	2 271(23)
C(123)	518(12)	5 954(15)	5 414(10)	C(3)	451(23)	6 943(32)	1 979(31)
C(124)	78(12)	6 679(15)	4 978(10)	C(4)	1 249(22)	7 463(33)	2 043(23)
C(125)	434(12)	7 174(15)	4 396(10)	C(5)	2 048(28)	6 668(28)	2 099(22)
C(126)	1 229(12)	6 944(15)	4 250(10)	C(6)	2 128(23)	5 852(32)	1 580(21)
P(2)	3 039(4)	2 911(5)	3 073(4)	C(7)	1 566(25)	5 632(31)	903(21)
C(201)	4 035(10)	2 368(14)	3 336(8)	C(8)	848(27)	4 942(40)	1 066(28)
C(202)	4 342(10)	2 506(14)	4 058(8)				

$F(000) = 2\,040$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 70.44 cm^{-1}.

Data collection and processing.[12] Stoe four-circle diffractometer, ω–2θ scan mode with a total ω scan width of 1.44°, scan speed 0.02—0.08° s^{-1}, graphite-monochromated Mo-K_α radiation; 5 492 reflections measured ($5.0 < 2\theta < 45.0°$, $\pm h$, $\pm k$, $+l$), 5 011 unique [merging R 0.071 after absorption correction using numerical methods and the crystal bounded by (100), ($\bar{1}$00), (011), (0$\bar{1}\bar{1}$), (01$\bar{1}$), and (0$\bar{1}$1) planes (maximum and minimum transmission factors 0.175 and 0.090)], giving 3 503 with $F > 5\sigma(F)$. Crystal deteriorated by *ca.* 23% in a relatively linear fashion during data collection and an appropriate correction was applied.

Structure analysis and refinement. Centrosymmetric direct methods (Ir, P, and Cl atoms) followed by Fourier difference techniques. Blocked-cascade least squares with Ir, P, Cl, and cyclo-octadiene C atoms anisotropic. Phenyl H and methylenic cyclo-octadiene H placed in idealised positions and allowed to ride 1.08 Å from the relevant C atom during refinement; each type of H assigned a common isotropic thermal parameter. Hydridic H atoms were not located directly but were placed in positions of minimum potential energy,[4] and were not included in refinements. The weighting scheme $w = [\sigma^2(F) + 0.0014|F|^2]^{-1}$ gave satisfactory agreement analyses. Final R and R' values are 0.082 and 0.082. Complex neutral atom scattering factors were employed,[13] and all computations were performed on an IBM 3081 computer at the University of Cambridge using a modified version of SHELX.[14] The final atomic fractional co-ordinates are listed in Table 3.

Acknowledgements

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