Formation of a Heterobimetallic Cyclohexa-1,4-dienyl-hydrido-complex from an Acetylide and Buta-1,3-diene: Crystal Structure of $[(p\text{-}MeC_6H_4C{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}H)Ir(CO)\{C{=}C(C_6H_3Me)CH_2CH{=}CHCH_2\}][BF_4]$ (dppm = $Ph_2PCH_2PPh_2$)

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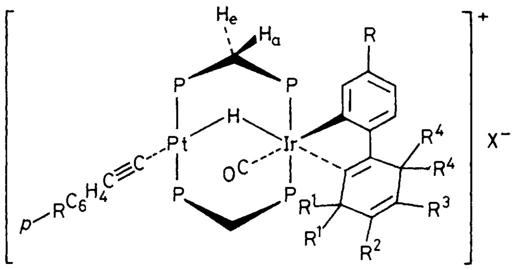
$[(p\text{-}MeC_6H_4C{\equiv}C)_2Pt(\mu\text{-}dppm)_2Ir(CO)][BF_4]$ (dppm = $Ph_2PCH_2PPh_2$) reacts with buta-1,3-diene to give the title compound in which a *p*-tolylacetylide ligand from platinum and a buta-1,3-diene on iridium have combined together to give the novel ligand in the title compound; isoprene and 1,1,4,4-tetradeuteriobuta-1,3-diene react similarly.

One of the aims of heterobimetallic chemistry is to use both metal centres, each having different kinds of reactivity, to effect a synthesis which would not occur on a single metal centre. In this communication we describe such a synthesis in which an acetylide group from one metal (platinum) and a diene system from a second metal (iridium) react together to form a novel ligand. We have described simple, high yielding syntheses of complexes of the type $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Ir(CO)]X$ (X = PF_6, BF_4, or BPh_4; dppm = $Ph_2PCH_2PPh_2$)[1] and have also shown previously[2] that buta-1,3-diene reacts with *trans*-$[IrCl(CO)(PMe_2Ph)_2]$, in the presence of large anions (BF_4^-, BPh_4^-, or ClO_4^-) to give adducts, formulated as $[Ir(CO)(PMe_2Ph)_2(\eta^4\text{-}C_4H_6)]X$, later confirmed by a crystal structure determination.[3] When we treated an acetone solution of $[(p\text{-}tolC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Ir(CO)][PF_6]$ (tol = MeC_6H_4) with butadiene at 20 °C the colour changed from orange to deep red-orange within 30 s and the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed that all the starting complex had reacted and a new complex, characterized by AA'BB' + AA'BB'M (M = ^{195}Pt) $^{31}P\text{-}\{^1H\}$ patterns, had formed: $\delta(P_A)$ 3.2, $\delta(P_B)$ −13.5 p.p.m., $^1J(PtP_A)$ = 2471 Hz, $|^2J(P_AP_B) + {}^4P(P_AP_{B'})|$ = '*N*' = 46 Hz. In this reaction the chemical shift of P_B (on Ir) had changed by *ca.* −25 p.p.m. from that of the starting complex whilst the chemical shift of P_A (on Pt) had hardly changed, suggesting that reaction had occurred at the iridium centre. We suggest this product was $[(p\text{-}tolC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Ir(CO)(\eta^4\text{-}C_4H_6)][PF_6]$ but it was not isolated as it changed gradually in solution into another species, conversion being complete in *ca.* 12 h, and no other phosphorus-containing product could be detected. This final product was isolated as brown microcrystals in 55% yield; elemental analysis suggested it was an adduct of the starting complex with butadiene and an electrical conductivity measurement showed it to be a uni-uni-electrolyte. The $^{31}P\text{-}\{^1H\}$ n.m.r. data were (in CD_2Cl_2) $\delta(P_A)$ 8.2, $\delta(P_B)$ −11.7 p.p.m., $^1J(PtP_A)$ 2451 Hz, '*N*' = 54 Hz. The ^1H and $^1H\text{-}\{^{31}P\}$ data showed the compound to contain a bridging hydride with δ_H −11.3 and $^1J(PtH)$ 535 Hz; the rest of the



(1)

a; R = Me; $R^1 = R^2 = R^3 = R^4 = H$; X = BF_4
b; R = Me, $R^1 = R^4 = D$; $R^2 = R^3 = H$; X = PF_6
c; R = Me, $R^1 = R^2 = R^4 = H$; $R^3 = Me$; X = PF_6
d; R = $R^1 = R^2 = R^3 = R^4 = H$; X = BPh_4

spectrum (see below) showed that an unusual reaction had occurred and therefore a crystal structure determination† was carried out on the corresponding BF_4 salt, prepared in an analogous manner to the PF_6 salt and grown from a dichloromethane–ethanol solution.

The structure is shown in Figure 1. The metal centres are linked by two *trans*-dppm bridges to give an eight-membered ring in the boat configuration. The platinum–iridium distance of 294.8(4) pm is longer than platinum–iridium bonds *ca.* 268—269 pm,[4] and this suggests that there is no significant platinum–iridium bonding. The most interesting feature of the structure is the substituted cyclohexa-1,4-dienyl ligand formed by the reaction of butadiene with one of the *p*-tolylacetylide ligands, originally attached to platinum, followed by *ortho*-metallation of the *p*-tolyl group, giving a bridging hydride and a novel chelate ligand. Although the bridging hydride ligand could not be detected by crystallography the n.m.r. data, given above, showed it to be present. The structure of the complex is shown diagrammatically in (**1a**). Additional ^1H n.m.r. data for (**1a**) are as follows: the dppm methylene groups showed pseudo-equatorial (H_e) [δ 4.97, $^3J(PtH_e)$ 75 Hz] and pseudo-axial hydrogen (H_a) [δ 4.32, ^3J too small to be observed, $^2J(H_eH_a)$ 13.5 Hz]. We have previously shown in other bis-dppm-platinum complexes that H_e is generally strongly coupled to platinum (a *transoid* coupling) whereas coupling to H_a cannot usually be detected.[5—7] Additionally, H_e is coupled to the bridging hydride ligand, $^4J(H_eH) = 3.1$ Hz (shown by selective decoupling experiments).

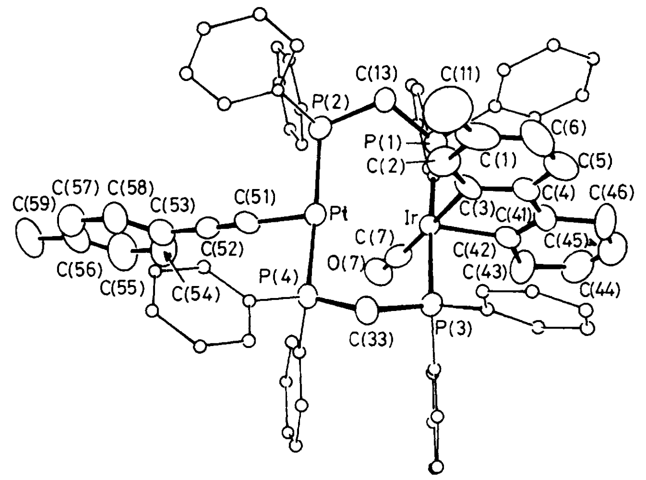


Figure 1. Crystal structure of $[(p\text{-tolC}{\equiv}\text{C})\text{Pt}(\mu\text{-dppm})_2(\mu\text{-H})\text{Ir}(\text{CO})\{\text{C}{=}\text{C}(\text{C}_6\text{H}_3\text{Me})\text{CH}_2\text{CH}{=}\text{CHCH}_2\}][\text{BF}_4]$ (**1a**). Ph groups on phosphorus have been omitted for clarity. Interatomic distances (pm) and angles (°): Pt(1)–Ir(1), 294.8(4); P(1)–Ir(1), 235.5(5); P(3)–Ir(1), 235.7(5); C(3)–Ir(1), 210.5(10); C(42)–Ir(1), 208.9(13); P(2)–Pt(1), 228.8(5); P(4)–Pt(1), 229.7(5); C(51)–Pt(1), 198.5(14); C(41)–C(4), 147.1(14); C(42)–C(41), 132.7(17); C(46)–C(41), 148.8(18); C(43)–C(42), 151.0(19); C(44)–C(43), 147.0(20); C(45)–C(44), 128.1(27); C(46)–C(45), 147.3(24); O(7)–C(7), 114.0(15); P(3)–Ir(1)–P(1), 169.3(1); C(3)–Ir(1)–P(1), 83.7(3); C(42)–Ir(1)–C(3), 79.0(5); C(7)–Ir(1)–C(3), 178.7(4); C(7)–Ir(1)–C(42), 100.3(5); P(4)–Pt(1)–P(2), 165.5(1); C(53)–C(52)–C(51), 179.0(11); C(42)–C(41)–C(4), 116.0(10); C(46)–C(41)–C(42), 122.6(12); C(43)–C(42)–C(41), 121.9(11); C(44)–C(43)–C(42), 113.6(13); C(45)–C(44)–C(43), 123.5(15); C(46)–C(45)–C(44), 124.4(16); C(45)–C(46)–C(41), 113.6(13); O(7)–C(7)–Ir(1), 176.1(9).

The six protons of the cyclohexadienyl ring of (**1a**) constitute an AA'MM'PX n.m.r. spin system, at 360 or 400 MHz, with small *J*-values. We assign the resonances as follows: δ 3.51 (H^4), 1.88 (H^1), 5.54 (H^2 or H^3), and 5.39 (H^3 or H^2); $^5J(H^1H^4)$ *ca.* 6, $^3J(H^2H^3)$ 10.0 Hz. 1,1,4,4-Tetradeuteriobutadiene, prepared by thermal decomposition of $[^2H_4]$butadiene sulphone (2,5-dihydrothiophene *S*,*S*-dioxide)[8] formed an adduct (**1b**) with an identical $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum to that of (**1a**). In the ^1H- or $^1H\text{-}\{^{31}P\}$ n.m.r. spectra, resonances due to H^1 and H^4 were absent whilst the resonances due to the other hydrogens were virtually the same as in the spectrum of (**1a**). The $^2H\text{-}\{^1H\}$ n.m.r. spectrum, measured at 55.28 MHz, showed two broad resonances at δ 3.5 and 1.9 p.p.m. Treatment of $[(p\text{-tolC}{\equiv}\text{C})_2\text{Pt}(\mu\text{-dppm})_2\text{Ir}(\text{CO})][\text{PF}_6]$ with 2-methylbuta-1,3-diene (isoprene) in refluxing acetone for 2 h gave an adduct, which on the basis of elemental analytical, electrical conductimetric, and n.m.r. data, was clearly analogous to the buta-1,3-diene adduct (**1a**). Moreover, only one isomer was produced, although the methyl group might have replaced a hydrogen in position 1 or position 2 of the cyclohexadienyl ring of (**1a**). The ^1H n.m.r. data showed the methyl group to be in position 3, *i.e.* the structure is (**1c**) since the resonance at δ 3.52 due to H^4 was a better-defined 1 : 2 : 1 triplet than with (**1a**) owing to the absence of any vicinal hydrogen, $^5J(^1H^4H) = 7.2$ Hz, whilst the pattern of the H^1 methylenes was a broader 1 : 2 : 1 triplet owing to a small coupling with the vicinal hydrogen and was very similar to that of (**1a**); the resonances due to H_e, H_a, and the hydride were similar to those of (**1a**), given above.

The cyclohexadienyl ring in complexes of type (**1**) might be formed by a Diels–Alder reaction between the acetylide group

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† *Crystal data:* $C_{73}H_{64}OP_4PtIr{\cdot}BF_4{\cdot}2CH_2Cl_2$, $M = 1725.54$, monoclinic, space group $P2_1/n$, $a = 1077.2(1)$, $b = 2574.9(3)$, $c = 2532.9(3)$ pm, $\beta = 94.94(1)°$, $U = 6.9995$ nm^3, $Z = 4$, $\mu = 40.1$ cm^{-1}, $F(000) = 3400$. Scans widths 1.8° + α doublet splitting, scan speeds 2.0—29.3° min^{-1} and $4.0 < 2\theta < 45.0°$. All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω/2θ scan mode using graphite monochromated Mo-K_α radiation following a procedure described elsewhere.[9] The data set was corrected for absorption empirically.[10] The structure was solved by standard heavy atom methods and refined by full-matrix least-squares using SHELX76.[11] All non-hydrogen atoms were refined anisotropically with all phenyl rings treated as rigid bodies with idealised hexagonal symmetry (C–H 139.5 pm). All phenyl-, methyl-, and methylene-hydrogen atoms were included in calculated positions (C–H 108 pm) and refined with an overall isotropic temperature factor. The weighting scheme $w = [\sigma^2(F_o) + 0.0008(F_o)^2]^{-1}$ was used at the end of refinement. Final R and R_w values are 0.0492 and 0.0506 respectively (688 parameters, 6710 observed data). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

and the diene. We suggest, however that it is formed by a sequence of steps: (i) transfer of acetylide from platinum to iridium, followed by (ii) the migration of the acetylide from iridium to the carbon of an η^2-bonded butadiene; (iii) a 1,3-allylic shift; (iv) a cylisation step, giving the hexa-1,4-diene ring, in which an allylic carbon becomes attached to one of the acetylenic carbons, and finally (v) ortho-metallation of the *p*-tolyl ring to give the chelate ring system and the bridging hydride ligand. The phenylacetylide complex, $[(PhC{\equiv}C)_2Pt(\mu\text{-dppm})_2Ir(CO)][PF_6]$ reacted with butadiene in an analogous manner to the *p*-tolylacetylide complex, giving (**1d**), but the methylacetylide complex reacted to give a complex mixture, which we have not identified.

We thank the S.E.R.C. for support, Johnson Matthey PLC for the generous loan of metal salts, and Dr. P. G. Pringle for preliminary work.

Received, 24th February 1987; Com. 250

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