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Ring Expansion in Dimetallacycle Chemistry: Preparation of a Dimetallacyclopentanol from a Dimetallacyclobutane

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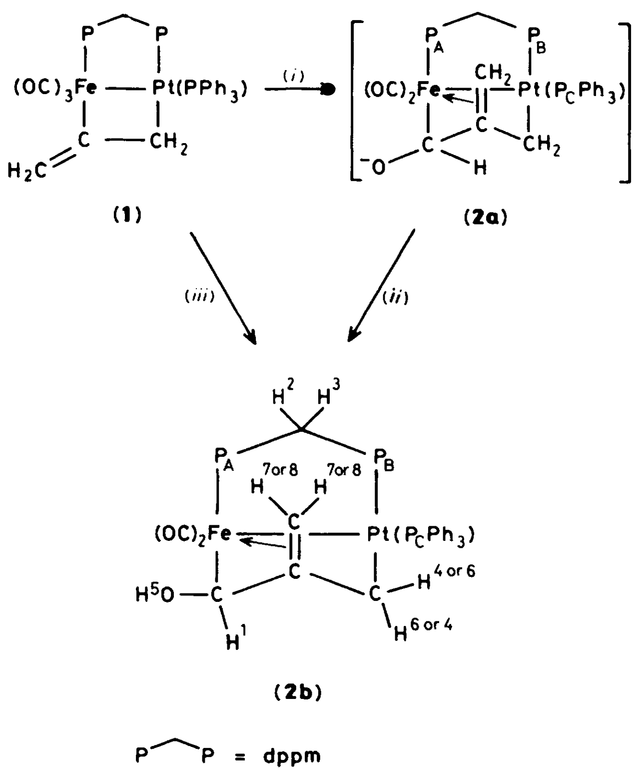
Treatment of the dimetallacyclobutane complex [$(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)$] (dppm = $Ph_2PCH_2PPh_2$) with an excess of $LiBHEt_3$ followed by methanol quantitatively gave the dimetallacyclopentanol complex [$(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}\sigma:\eta^3\text{-}CH(OH)C(=CH_2)CH_2\}Pt(PPh_3)$].

In recent publications we have described the preparation and chemistry of the dimetallacyclobutane complex [$(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)$] (**1**) (dppm = $Ph_2PCH_2PPh_2$), formed by treating [$(OC)_3Fe(\mu\text{-dppm})(\mu\text{-}CO)Pt(PPh_3)$] with allene.[1,2] In this work we report that (**1**) can be converted, quantitatively, *via* a novel carbonyl reduction/ring expansion reaction, into a dimetallacyclopentanol system.

Results and Discussion

Treatment of a tetrahydrofuran (thf) suspension/solution of compound (**1**) with an excess of $LiBHEt_3$ in thf gave a single, new, heterobimetallic species (**2a**) in which the basic metal–phosphine backbone was retained ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence). This species was very reactive and was not isolated. However, addition of an excess of MeOH (or water) to this solution resulted in the quantitative formation of a second species (**2b**) again with retention of the metal–phosphine backbone ($^{31}P\text{-}\{^1H\}$ n.m.r. evidence). Compound (**2b**) was also formed when (**1**) was treated with $NaBH_4$ in thf. It was isolated as a yellow, air-sensitive, microcrystalline solid in 70% yield, and characterised by elemental analysis, i.r., and $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. spectroscopy (see Experimental section for details and the Scheme for assignments).



Scheme. (*i*) $LiBHEt_3$, thf; (*ii*) MeOH or water; (*iii*) $NaBH_4$, thf

Examination of the 400-MHz ^1H n.m.r. spectrum of (**2b**) (see Figure) shows the complex to contain eight non-equivalent non-phenyl protons. Two of these (AB spin system at 4.25 and 4.13 p.p.m.) are assigned to the non-equivalent dppm methylene protons, H(2) and H(3), one of which is coupled to platinum-195. The remaining six protons must arise from the organic ligand and since complex (**1**) contains only four allene protons it is likely that the other two have come from the sequential addition of H^- (from $LiBHEt_3$ or $NaBH_4$) and H^+ (from MeOH or water). In order to accommodate six non-equivalent protons an extra carbon must be incorporated into the allene ligand of (**1**) and we propose that this comes from one of the carbonyl ligands on iron. Activation of iron carbonyls with sources of hydride is well known,[3,4] and in this case a metal formyl is probably formed, initially. This could then rearrange by a ring expansion to give the alkoxide (**2a**) as shown in the Scheme. Protonation of the oxygen atom of (**2a**) would then give the alcohol (**2b**).

The details of the ^1H n.m.r. spectrum of complex (**2b**) are in agreement with the proposed structure. The broad resonance at 2.30 p.p.m. disappears on addition of D_2O and thus is assigned to the hydroxy proton, H(5). The $^1H\text{–}^1H$ COSY spectrum with ^{31}P decoupling (Figure) shows that this hydroxy proton is weakly coupled to H(1) at 5.18 p.p.m. which is thus assigned to C*H*(OH). The strongly mutually coupled protons at 2.86 and 1.99 p.p.m. are assigned to the non-equivalent Pt–CH_2 protons, H(4) and H(6). Their large couplings to platinum [*J*(PtH) 65 and 78 Hz] and their couplings to the phosphorus atoms on platinum (P_B and P_C) support these assignments. The remaining two resonances are weakly mutually coupled (COSY evidence); only one, H(8), is coupled to platinum [*J*(PtH) 25 Hz] and weakly coupled to P_C. The other, H(7), is coupled only to the phosphorus atom on iron, P_A. The COSY spectrum also shows that H(4) is weakly coupled to H(8). An alternative structure for the reduction product, in which a carbonyl ligand in (**1**) has been converted into a hydroxycarbene [=C(OH)H] leaving the bridging allene intact, can be effectively ruled out because of the absence of the two vinylic proton resonances in the ^1H n.m.r. spectrum, which for (**1**) occur at 5.52 and 5.11 p.p.m. Also, such a hydroxycarbene group might be expected to be very unstable.

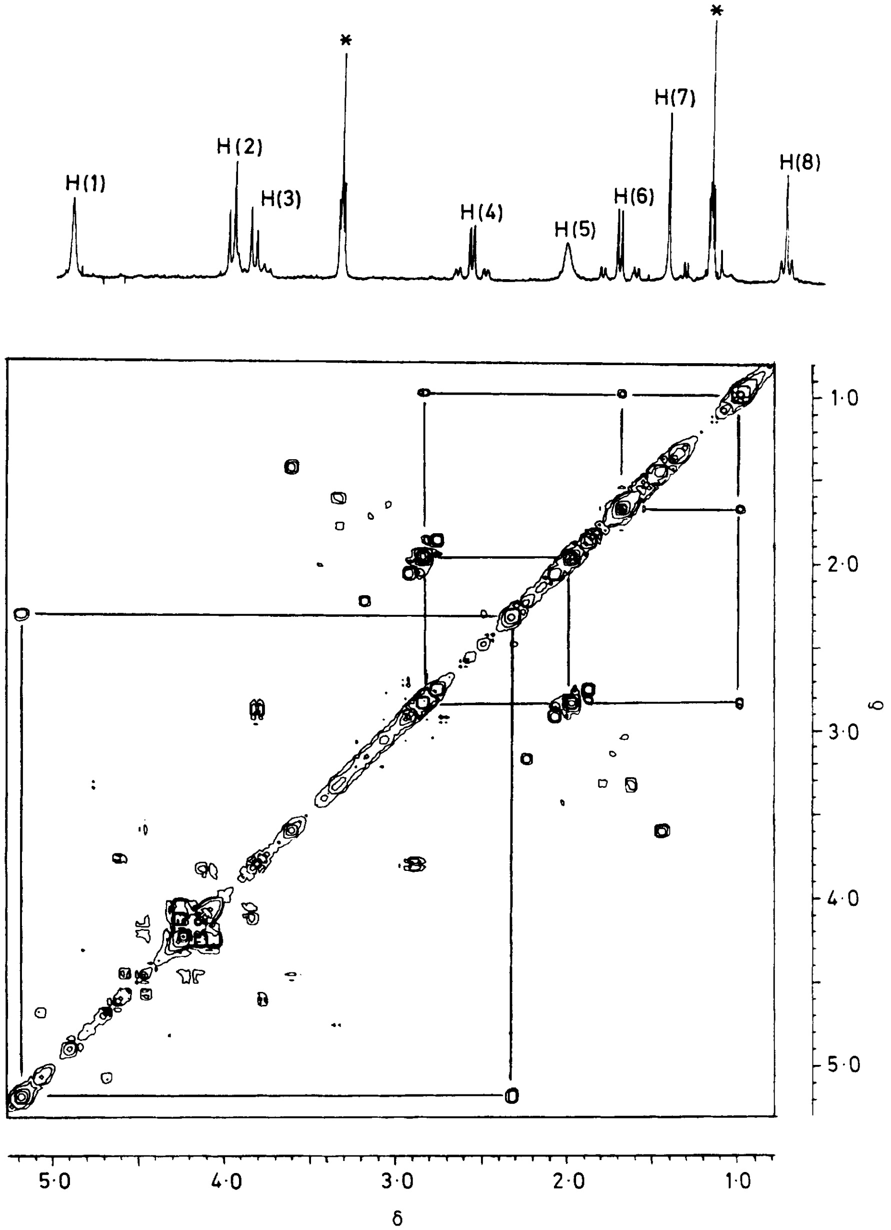


Figure. Part of the 400-MHz $^{1}H\text{-}\{^{31}P\}$ n.m.r. spectrum and $^{1}H\text{-}^{1}H$ COSY spectrum (with ^{31}P decoupling) of compound (**2b**), recorded in C_6D_6. The peaks marked with an asterisk are due to tetrahydrofuran

The $^{31}P\text{-}\{^{1}H\}$ n.m.r. spectra of compounds (**2a**) and (**2b**) are very similar, suggesting closely related structures. In (**2b**), the olefin function probably makes a π interaction with the iron atom in order to raise the electron count to eighteen. The i.r. spectrum (CH_2Cl_2 solution) supports this in that it shows only two bands attributable to terminal ν(CO). The organic ligand in (**2b**) can therefore be regarded as a three-electron donor to iron and a one-electron donor to platinum.

Other, related complexes, *viz.* $[(OC)_3Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]$, $[(OC)_2Fe(\mu\text{-dppm})(\mu\text{-CO})Pt(PPh_3)]$, $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}\sigma:\eta^3\text{-}C(O)C_2H_2\}Pt(PPh_3)]$, and $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(O)CH_2C(=CH_2)\}Pt(PPh_3)]$, do not react cleanly with $LiBHEt_3$ to give new heterobimetallic complexes. Compound (**1**) therefore, appears to be a special case, possibly because of the availability of the vinylic function to take up the vacant co-ordination site on iron.

Experimental

General methods were as previously described in recent papers from this laboratory.[5]

Preparation of $[(OC)_2Fe(\mu\text{-dppm})\{\mu\text{-}\sigma:\eta^3\text{-}CH(OH)C(=CH_2)CH_2\}Pt(PPh_3)]$ (**2b**).—An excess of $LiBHEt_3$ [0.5 mmol in thf (0.5 cm^3)] was added to a solution/suspension of $[(OC)_3Fe(\mu\text{-dppm})\{\mu\text{-}C(=CH_2)CH_2\}Pt(PPh_3)]$ (0.1 g, 0.1 mmol) in thf (4 cm^3). All the solid dissolved to give an orange solution. This was reduced in volume to *ca.* 1.5 cm^3 and MeOH (2 cm^3) was added. The resultant yellow-brown solution was refrigerated (− 20 °C) for *ca.* 16 h to give the desired product, as bright yellow microcrystals. Yield 0.07 g (70%), ν(CO) (in CH_2Cl_2) at 1 942s and 1 880m cm^{-1}. N.m.r. (C_6D_6): ^{1}H, δ 5.18 [s, 1 H, H(1)], 4.25 [AB, 1 H, H(2) or H(3), *J*(HH) 14], 4.13 [AB, 1 H, H(2) or H(3), *J*(HH) 14, *J*(PtH) 60], 2.86 [d of d of d, 1 H, H(4) or H(6), J(HH) 10, J(P_BH) 15, J(P_CH) 7, J(PtH) 65], 2.30 [s, br, 1 H, H(5)], 1.99 [d of d of d, 1 H, H(4) or H(6), J(HH) 10, J(P_BH) 10, J(P_CH) 10, J(PtH) 78], 1.71 [d, 1 H, H(7) or H(8), J(P_AH) 5], and 1.05 [d, 1 H, H(7) or H(8), J(P_CH) 2, J(PtH) 25]; $^{31}P-\{^1H\}$, δ 63.4 [d of d, P_A, $J(P_AP_B)$ 115, $J(P_AP_C)$ 37, $J(PtP_A)$ 88], 21.4 [d, P_C, $J(P_AP_C)$ 37, $J(PtP_C)$ 2 570], and 3.3 [d, P_B, $J(P_AP_B)$ 115, $J(PtP_B)$ 2 700 Hz] (Found: C, 56.85; H, 4.5. $C_{49}H_{43}FeO_3P_3Pt$ requires C, 57.5; H, 4.25%).

$^{31}P-\{^1H\}$ N.m.r. data for **(2a)**: δ 71.9 [d of d, P_A, $J(P_AP_B)$ 137, $J(P_AP_C)$ 37], 20.1 [d, P_C, $J(P_AP_C)$ 37, $J(PtP_C)$ 2 251], and 8.6 [d, P_B, $J(P_AP_B)$ 137, $J(PtP_B)$ 2 544 Hz].

Acknowledgements

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