Preparation and Structure of [Rh{(η^5-C_5H_4(2-C_5H_4N))(η^5-$C_5H_4PPh_2$)}(cod)]PF_6 and [Ir(H){Fe[η^5-C_5H_3(2-C_5H_4N)](η^5-$C_5H_4PPh_2$)}(cod)]PF_6; a Rh^I complex having a C–H · · · Rh^I Interaction and a Hydrido Ir^{III} Complex (where cod = cyclo-octa-1,5-diene)

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A rhodium complex (**2**) of [Fe{η^5-C_5H_4(2-C_5H_4N)}(η^5-$C_5H_4PPh_2$)] contains a C–H · · · Rh^I interaction, which shows a marked high-frequency shift in the ^1H NMR spectrum, whereas the corresponding iridium complex forms an iridium(III) hydrido complex (**3**), resulting from the oxidative addition of the C–H bond.

Many examples of transition metal complexes showing carbon–hydrogen–metal interactions have been recognized.[1] However it is rare that both an intermediate complex containing an activated C–H bond interacting with metal and the corresponding hydrido complex resulting from the oxidative addition of the C–H bond are isolated.

By a conventional reaction of [M(cod)Cl]$_2$ (M = Rh, Ir; cod = cyclo-octa-1,5-diene) with a new ferrocenylphosphinepyridine ligand, [Fe{η^5-C_5H_4(2-C_5H_4N)}(η^5-$C_5H_4PPh_2$)] (**1**)† in

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† All new complexes show satisfactory elemental analyses and spectroscopic data.

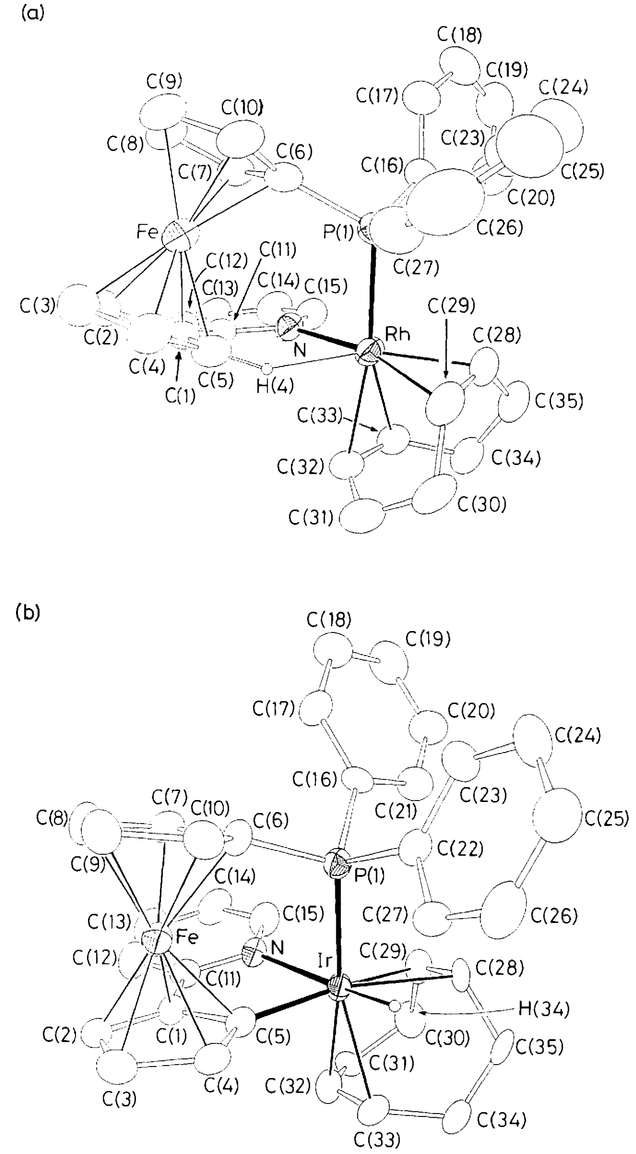

Figure 1. (a) ORTEP drawing of the cationic part of (**2**) (50% probability ellipsoids), selected bond lengths (Å) and angles (°): Rh–P(1) 2.326(2), Rh–N 2.136(4), Rh–C(28) 2.16(1), Rh–C(29) 2.163(6), Rh–C(32) 2.22(1), Rh–C(33) 2.248(6), Rh–C(5) 3.110(6), Rh–H(4) 2.39(5); P(1)–Rh–N 92.3(1), P(1)–Rh–CEN(1) 93.2(1), P(1)–Rh–CEN(2) 176.6(1), N–Rh–CEN(1) 171.3(2), N–Rh–CEN(2) 88.5(2), CEN(1)–Rh–CEN(2) 85.7(2). [CEN(1) and CEN(2) denote the centre of C(28) and C(29) and that of C(32) and C(33), respectively.] (b) ORTEP drawing of the cationic part of (**3**) (50% probability ellipsoids). Selected bond lengths (Å) and angles(°): Ir–P(1) 2.334(3), Ir–N 2.233(8), Ir–C(5) 2.03(1), Ir–C(28) 2.28(1), Ir–C(29) 2.31(1), Ir–C(32) 2.27(1), Ir–C(33) 2.30(1); P(1)–Ir–N 92.3(2), P(1)–Ir–C(5) 88.5(3), P(1)–Ir–CEN(1) 98.2(2), P(1)–Ir–CEN(2) 168.6(2), C(5)–Ir–N 78.6(3), CEN(1)–Ir–CEN(2) 82.6(3). [CEN(1) and CEN(2) denote the centre of C(28) and C(29) and that of C(32) and C(33), respectively.]

the presence of $AgPF_6$, cationic complexes having the same composition [M(cod)(**1**)]PF_6 [(**2**) M = Rh; (**3**) M = Ir]† but different structures, have been prepared in good yield. The structures of these complexes have been elucidated mainly by ^1H NMR spectroscopy (500 MHz) involving ^1H COSY and difference NOE methods and proposed to be square planar rhodium(I) and octahedral hydrido iridium(III) complexes, respectively. In the irradiation experiments of (**2**), spin saturation transfers between the signals of δ 2.75 and 4.51 [assigned to the β-protons of the cyclopentadienyl (cp) ring carrying a PPh_2 group] and those of δ 7.82 and 4.92 [assigned to the β-protons of the cp ring carrying a 2-pyridyl group, cp(N)] were observed, which indicate that these protons are exchanging slowly in solution as shown in equation (1). This exchange may be caused by dissociation of the co-ordinated pyridyl nitrogen. The exchange rate constant was estimated to be *k* 1.8 s^{-1}.[3] The very high-frequency shifts for ^1H (Δδ 3.09) and ^{13}C (Δδ 71.3) of one of the cp C–H bonds compared to those of the free ligand (**1**) are characteristic. These can be considered as a result of the C–H bond being strongly deshielded due to donation of the electron density of the C–H bond to the central rhodium(I) and to show the proton locating very closely to the rhodium atom. Such high-frequency shift of the proton signal for a proton located closely to a metal has been recognized in several complexes.[4] However, the $^1J_{CH}$ value (170 Hz) is not diminished significantly relative to the free ligand ($^1J_{CH}$ 176 Hz). This is very much different from the case found for a C–H bond showing a usual agostic interaction.[1]

Unlike (**2**), the ^1H NMR (δ −13.8, 1H, $^2J_{P\text{-}H}$ 9.4 Hz) and the IR spectra ($\nu_{Ir\text{-}H}$ 2260 cm^{-1}) of (**3**) indicate the presence of a metal hydride, the hydrido ligand being located in the *cis* position to the phosphorus atom as judged by the coupling constant.[5] The selective formation of only one isomer (**3**) for the iridium hydrido complex can be understood from the steric requirement of the ligand (**1**) and the different *trans* influence between phosphorus and nitrogen.

The proposed structures for (**2**) and (**3**) have been confirmed by *X*-ray analyses‡ (Figure 1). The location of one of the cp protons close to the rhodium atom in the complex (**2**) suggested from ^1H NMR has also been verified by a short distance between one of the β-protons of the cp(N) and the Rh atom [Rh–H 2.39(5) Å]; the proton occupies the fifth co-ordination site and the complex forms a pseudo square pyramid. In view of the present data, we believe that the complex (**2**) contains only a weak C–H · · · Rh interaction. Consistently, the corresponding rhodium hydrido complex could not be obtained even after heating a CH_2Cl_2 solution of (**2**) in an autoclave at 70 °C for 18 h. Thus the reaction of (**1**) with Rh^I forms a Rh^I complex (**2**), in which a C–H bond of

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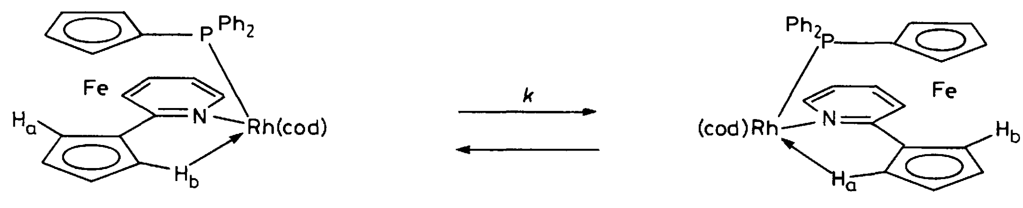
‡ *Crystal data* for (**2**): $C_{35}H_{34}F_6FeNP_2Rh$, *M* = 803.32, monoclinic, space group $P2_1/c$, *a* = 14.079(7), *b* = 11.266(4), *c* = 20.599(11) Å, β = 92.93(5)°, *U* = 3263(3) Å^3, *Z* = 4, D_c = 1.636 g cm^{-3}, μ(Mo-K_α) = 92.6 cm^{-1}, crystal size = 0.6 × 0.4 × 0.4 mm. For (**3**): $C_{35}H_{34}F_6FeNP_2Ir$, *M* = 892.66, monoclinic, space group $P2_1/c$, *a* = 14.224(8), *b* = 11.492(2), *c* = 19.613(6) Å, β = 101.81(3)°, *U* = 3138(2) Å^3, *Z* = 4, D_c = 1.890 g cm^{-3}, μ(Mo-K_α) = 133.2 cm^{-1}, crystal size = 0.6 × 0.3 × 0.1 mm. Data were collected on a Rigaku Denki AFC-4 automated diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å) using ω–2θ scan [$2\theta_{max.}$ <50° for (**2**) and 55° for (**3**)]. The structure was solved by direct method and difference-Fourier techniques, and all non-hydrogen atoms were refined with anisotropic thermal parameters by block-diagonal least squares methods. For (**2**), the positions of all hydrogen atoms were refined. Final *R* value for (**2**) was 0.0350, R_w = 0.0381 ($w = 1/\sigma^2$) for 3584 (>5σ) reflections. For (**3**), all hydrogen atoms of ligands were fixed to the calculated positions. A difference Fourier map calculated with limited data set (sin θ/λ <0.30) showed two large peaks near the Ir atom, one of which, completing the octahedral co-ordination around the Ir atom, was assigned as a hydrido ligand. The hydride was fixed in this position. The final *R* value for (**3**) was 0.0433, R_w = 0.0439 ($w = 1/\sigma^2$) for 4190 (>5σ) reflections. 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.



(1)

cp(N) is interacting with the rhodium metal but only weakly activated, whereas the reaction of (**1**) with iridium(I) complex results in facile oxidative addition of the C–H bond to give an Ir^{III} hydride (**3**). This marked difference between rhodium and iridium complexes may partly arise from the difference between thermodynamic stability of their hydrido complexes.[6] These rhodium and iridium complexes of the ferrocenylphosphinepyridine (**1**) provide a rare example of a pair of complexes for C–H activation with a transition metal, resulting in formation of an oxidative addition product and visualize a course for an oxidative addition of an intramolecular C–H bond.

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