Synthesis, Reactions and Catalytic Activities of Cationic Iridium(I) Complexes of Cycloocta-1,5-diene†

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New cationic iridium(I) complexes, $[Ir(cod)(PPh_3)L]ClO_4$ **1** [cod = cycloocta-1,5-diene; L = PhCN, PhCH=CHCN, CH_2=CHCN, CH_2=C(Me)CN, MeCH=CHCN or CH_2=$CHCH_2CN$ co-ordinated through the nitrogen atom], have been prepared by the reactions of $[IrCl(cod)(PPh_3)]$ with $AgClO_4$ in the presence of L. Reaction of $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **1a** with H_2 gives the *cis*-dihydridoiridium(III) complex $[IrH_2(cod)(PPh_3)(PhCN)]ClO_4$ **2a** where the two hydrides are *trans* to PhCN and an olefinic group of cod, respectively. Complex **2a** is stable both in solution and in the solid state at low temperature and decomposes at 15 °C to give cyclooctane and unidentified Ir–cod complex(es). The nitrile (L) in **1** is readily replaced by both PPh_3 and CO, while cod is replaced only by CO. In the presence of complexes **1**, unsaturated alcohols such as CH_2=$CHCH_2OH$, CH_2=CHCH(Me)OH and CH_2=CHCH(Ph)OH rapidly undergo isomerization to the corresponding saturated carbonyl compounds at room temperature. Complex **1a** catalyses the hydrogenation of unsaturated aldehydes, PhCH=CRCHO (R = H, Me or Cl) to give $PhCH=CRCH_2OH$, $PhCH_2CHRCHO$ and $PhCH_2CHRCH_2OH$ under H_2 (p_{H_2} = 6 atm) at 50 °C.

Iridium(I) complexes of cycloocta-1,5-diene (cod) have been of interest for chemists probably because co-ordinated cod is readily replaced with other ligands to give new compounds[1] and hydrogenated with H_2 to provide vacant co-ordination sites around iridium and a subsequent increase in the catalytic activities of the complexes.[2] The complex $[Ir(cod)(py)\{P(C_6H_{11})_3\}]^+$ (py = pyridine) is known to catalyse hydrogenation of the olefinic group of unsaturated alcohols to give stereoselective hydrogenation products due to the interaction between the metal and hydroxyl group.[2b,c] Similar complexes $[Ir(cod)(P–N)]^+$ (P–N = chelate ligands with phosphorus and nitrogen base atoms) have recently been reported, having catalytic activities for N–H bond activation.[1a] While a large number of cationic iridium(I) complexes, $[Ir(cod)L_2]^+$ [L_2 = $(PR_3)_2$, P–P (chelate ligands with two phosphorus base atoms), $(nitrile)_2$ or N–N (chelate ligands with two nitrogen base atoms)][1d,2d,3] have been extensively studied, only a few complexes $[Ir(cod)L(L')]^+$ (L = phosphorus base ligand, L' = nitrogen base ligand)[2b,c] and $[Ir(cod)(P–N)]^+$ (P–N = bidentate ligand with phosphorus and nitrogen base atoms)[1a] have been synthesised. We have prepared new cationic iridium(I) complexes, $[Ir(cod)(PPh_3)L]ClO_4$ (L = PhCN or unsaturated nitrile), and investigated their reactions with H_2 and catalytic activities for reactions of unsaturated alcohols. Rhodium analogues, $[Rh(cod)(PPh_3)L]^+$ (L = nitrile), have been reported previously.[4]

Results and Discussion

Synthesis.—The complexes $[Ir(cod)(PPh_3)L]ClO_4$ **1** (L = nitrile) have been prepared according to Scheme 1. Attempts to isolate the complexes of saturated nitriles such as MeCN and EtCN were unsuccessful for unknown reasons.

$$[IrCl(cod)(PPh_3)] + L \xrightarrow[-AgCl]{AgClO_4} \underset{\mathbf{1}}{[Ir(cod)(PPh_3)L]ClO_4} \quad (1)$$

Scheme 1 L = PhCN **a**, *trans*-PhCH=CHCN **b**, CH_2=CHCN **c**, CH_2=C(Me)CN **d**, MeCH=CHCN **e** (mixture of *cis* and *trans* isomers), or CH_2=$CHCH_2CN$ **f**

† *Non-SI unit employed:* atm = 101 325 Pa.

Infrared spectral data are very useful to characterize the bonding of nitrile groups.[5] It is evident that the nitriles (L) in complexes **1** are all co-ordinated through the nitrogen atom, but not through the π system of either the nitrile or olefinic group since ν(C≡N) are considerably higher than those of free L, while ν(C=C) do not show significant changes from those of free L (see Experimental section). A broad and strong absorption is observed for all **1** at *ca.* 1100 cm^{-1} which is attributed to a non-co-ordinating ClO_4^- group.[6] Proton NMR spectral data also support the absence of bonding between Ir and the olefinic group of L in **1** since the chemical shifts for the olefinic protons are not shifted much from those of free L (see Experimental section). Unsaturated nitriles co-ordinated to metals through the olefinic group show considerable upfield shifts of the olefinic protons relative to those of the free ligands[5,7] whereas relatively small, up- or down-field, shifts have been observed for metal–nitrogen bonded complexes of unsaturated nitriles.[5,8] Electronic absorption spectra of complexes **1** show three absorption bands (see Experimental section) as observed for many related iridium(I) complexes, [IrCl(diene)(MeCN)] [diene = cod or norbornadiene (nbd)],[9] $[Ir(diene)(bipy)]^+$ (diene = cod or nbd; bipy = 2,2'-bipyridyl)[10] and $[IrA(CO)(PPh_3)_2]$ (A = anionic monodentate ligand with various ligating atoms).[11] Conductivity measurements confirm **1** as being 1:1 electrolytes (see Experimental section).

Reactions.—Complex **1a** rapidly reacts with H_2 to give a dihydridoiridium(III) complex $[IrH_2(cod)(PPh_3)(PhCN)]ClO_4$ **2a** which can be isolated only at low temperature (−78 °C). It is evident that the other compounds, **1b–1f**, also react with H_2 to give the corresponding dihydridoiridium(III) complexes, their orange colour disappearing immediately when H_2 is bubbled into a solution in $CHCl_3$. Attempts to isolate any dihydrido complexes at room temperature were unsuccessful (see below). Detailed ^1H NMR spectral data measured for **2a** suggest that the two hydrides are *cis* to each other and *trans* to cod and PhCN, respectively (see structure **I**). The spectrum measured at −50 °C in $CDCl_3$ shows two doublets at δ −15.96 (H_A) and −13.20 (H_B) with different coupling constants, 13.4 and 18.3 Hz, respectively (see Fig. 1). The coupling constants between hydride and *trans* phosphorus are relatively large (53–154 Hz)

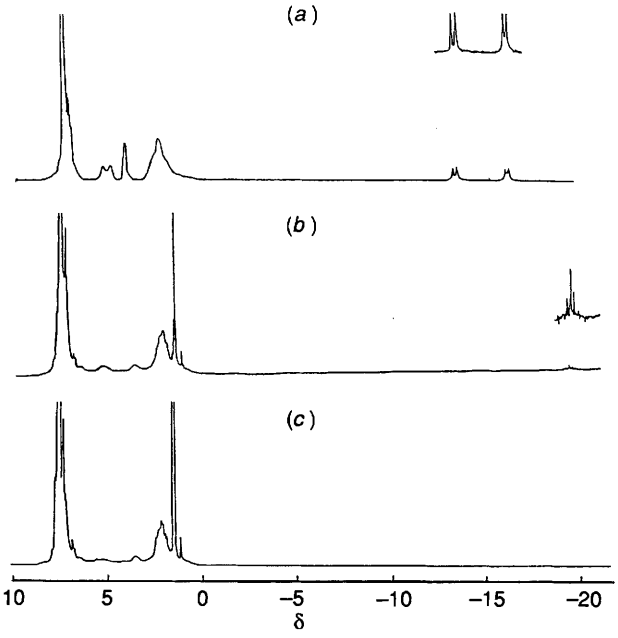
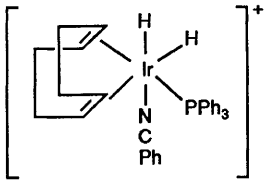


Fig. 1 Proton NMR spectra at 80 MHz of $[IrH_2(cod)(PPh_3)(PhCN)]ClO_4$ **2a** in $CDCl_3$ under N_2 (*a*) at −50 °C, (*b*) after 30 min at 15 °C and (*c*) after 1 h at 15 °C

compared with those between hydride and *cis* phosphorus (10–20 Hz).[8a,12] Accordingly, the two doublets at δ −15.96 and −13.20 are assigned to two inequivalent hydrides, H_A and H_B, both of which are *cis* to PPh_3. It is well known that the chemical shift of a hydride co-ordinated to a transition metal largely depends on the *trans* donor atom.[12,13] The shielding at a hydride *trans* to a nitrogen atom is higher (δ −17 to −20)[8a,12c,13a] than that at a hydride *trans* to a carbon atom (δ −7 to −14).[8a,12d,13b] The doublet at δ −13.7 was unambiguously assigned to the hydride *trans* to cod in $[IrH_2(cod)(PMePh_2)_2]^+$.[12a] The doublet at δ −13.20 observed for **2a** is now assigned to the hydride (H_B) *trans* to cod and that at δ −15.96 to H_A *trans* to PhCN (see structure **I**). Multiplets due to cod protons are seen at δ 2.0–5.8 and the protons of PPh_3 and PhCN show signals at δ 7.0–8.0.



I

The infrared spectrum (Nujol) of complex **2a** shows a strong absorption at 2137 cm^{-1} and a medium absorption at 2253 cm^{-1} [a weak and sharp ν(C≡N) absorption might be overlapped with this band] due to Ir–H stretching modes. The corresponding spectrum of $[IrD_2(cod)(PPh_3)(PhCN)]ClO_4$ **2a′** prepared in the same manner as described for **2a** (see Experimental section) shows a weak and sharp ν(C≡N) absorption at 2265 cm^{-1} (Nujol) [weak–medium band at 1540 cm^{-1} may be assigned to ν(Ir–D)]. It is well known that related *cis*-dihydridoiridium(III) compounds show two unsymmetric absorption bands at 2100–2250 cm^{-1}.[8a,14] A strong and broad band observed at *ca.* 1100 cm^{-1} is assigned to a non-co-ordinating ClO_4^- group,[6] which supports **2a** as being a 1:1 electrolyte. It should be mentioned that compound **2a** is so unstable that it rapidly decomposes even in the solid state to unknown compounds. The infrared spectral data for **2a** were obtained by using a fresh sample immediately after preparation at low temperature under hydrogen (see Experimental section).

It is surprising that decomposition of complex **2a** in solution in the absence of excess of H_2 (under N_2) gives cyclooctane and unknown iridium–cod complex(es). Cyclooctane may well be the product of a bimolecular process between two molecules of the iridium complex. The hydrogen (H_2) concentration in the reaction mixture would not be high enough for further hydrogenation of cyclooctene (C_8H_{14}) formed by intramolecular hydrogen transfer in **2a** even if it is possible that a part of **2a** liberates H_2 in the reaction mixture (see Experimental section). A trihydride-bridged binuclear iridium(III) complex, $[L_2HIr(\mu\text{-}H)_3IrHL_2]^+$ (L = PPh_3) and a trinuclear iridium(III) complex of a triply bridging hydride, $[\{IrH_2L(L')\}_3(\mu_3\text{-}H)]^{2+}$ (L = PR_3, L′ = py) are formed along with cyclooctane in the reactions of mononuclear iridium(I) complexes of cod, $[Ir(cod)L_2]^+$ and $[Ir(cod)L(L)]^+$, with excess of H_2.[15] These observations led us to suggest a bimolecular process forming a dihydride-bridged complex, cyclooctane and unknown Ir–cod complex(es). The triplet-like hydride signals at δ −19.11 observed during the formation of cyclooctane (C_8H_{16}) [see Fig. 1(*b*)] may be due to the bridging hydrides of the binuclear complex. In the presence of excess of H_2 (atmospheric pressure) at room temperature, complex **1** in $CDCl_3$ gives C_8H_{16} quantitatively and black unidentified iridium complex(es). No evidence has been found for hydrogenation of co-ordinated unsaturated nitriles in **1b–1f** under atmospheric pressure of H_2 at room temperature.

The cod in complexes **1** is not replaced with excess of PPh_3 under refluxing conditions in benzene, whereas the unsaturated nitriles in **1a** and **1c–1f** are readily substituted by PPh_3 to give $[Ir(cod)(PPh_3)_2]ClO_4$[1d,2e] [equation (2)]. The PhCH=CHCN in **1b** is not replaced with PPh_3 under reflux conditions, probably due to the poor solubility of **1b** in benzene. Reactions of **1** with CO seem to be somewhat complicated. The nitrile, L, and cod of **1** are replaced by CO to produce unidentified iridium complex(es) whose IR and ^1H NMR spectra clearly suggest an $Ir(CO)_x(PPh_3)$ moiety: L is first replaced by CO and then cod is slowly substituted by CO (see Experimental section).

$$[Ir(cod)(PPh_3)L]ClO_4 + PPh_3 \xrightarrow[C_6H_6]{\text{reflux}} \underset{\textbf{1a, 1c–1f}}{} [Ir(cod)(PPh_3)_2]ClO_4 + L \quad (2)$$

Catalytic Activities.—Complex **1a** (and **1c–1f**) rapidly catalyses the isomerization of some unsaturated alcohols to the corresponding carbonyl compounds at room temperature. The isomerization [equation (3)] apparently consists of two steps,

$$CH_2{=}CHCHROH \xrightarrow[(3:1 = 1000:1)]{\textbf{1}, 25\ ^\circ C, 1.0\ h} MeCH_2C(O)R \quad (3)$$

R = H, Me or Ph

$$CH_2{=}CHCHROH \xrightarrow{\textbf{1}} MeCH{=}CROH \longrightarrow MeCH_2C(O)R \quad (4)$$

double-bond migration to give the enols and ketonization of the enols [equation (4)] as observed for related iridium and rhodium complexes.[16] A considerable amount of the enol MeCH=CHOH[17] (mixture of *E* and *Z* isomers) was detected during the isomerization of $CH_2{=}CHCH_2OH$ to $MeCH_2CHO$ with **1a** in the absence of a solvent. The corresponding enols MeCH=CROH (R = Me or Ph) have not been detected during the isomerization (3) although the isomerization rates of $CH_2CH{=}CHROH$ to give $MeCH_2C(O)R$ (R = Me or Ph) are somewhat faster than that of $CH_2{=}CHCH_2OH$ to $MeCH_2CHO$ under same experimental conditions (see Experimental section). These observations may be understood by the relative

$$PhCH{=}CRCHO \xrightarrow{(i)} PhCH{=}CRCH_2OH + PhCH_2CHRCHO + PhCH_2CHRCH_2OH \quad (5)$$

Scheme 2 (*i*) $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ (1:150) in $CDCl_3$, P_{H_2} = 9 atm, 50 °C, 3 h. Yields: R = H, $PhCH_2CH_2CHO$, 84; $PhCH_2CH_2CH_2OH$, 16; R = Me, $PhCH{=}C(Me)CH_2OH$, 47; $PhCH_2CH(Me)CHO$, 6; $PhCH_2CH(Me)CH_2OH$, 40; $PhCH_2CHMe_2$, 7; R = Cl, $PhCH{=}CClCH_2OH$, 93; $PhCH_2CHClMe$, 4; $PhCH{=}CClCHO$, 3; small amount of unidentified oligomers

ketonization rates of $MeCH{=}CROH$. Similar results were obtained and discussed in detail for the isomerization of unsaturated alcohols with rhodium(I) and iridium(I) complexes.[16a]

Double-bond migration in *cis*-$HOCH_2CH{=}CHCH_2OH$ (followed by rapid ketonization) is also catalysed by complex **1a** to generate $HOCH_2CH_2CH_2CHO$ which undergoes cyclization to give 2-hydroxytetrahydrofuran, $\overline{OCH_2CH_2CH_2CH(OH)}$, which was recently observed with rhodium(I) complexes[18] (see Experimental section for details). It is striking that very similar unsaturated alcohols, $CH_2{=}C(Me)CH_2OH$, $CH_2{=}C(Me)CH(Me)OH$ and $CH_2{=}C(Me)CH(Ph)OH$ do not undergo isomerization to the carbonyl compounds in the presence of **1** at room temperature (probably too slow to be detected). This is certainly not due to the steric effects of the substituents since it is well known that isomerization of $CH_2{=}C(Me)CH_2OH$ to Me_2CHCHO by $[Rh(CO)(PPh_3)_3]ClO_4$ is so fast that the intermediate enol, $Me_2C{=}CHOH$, could be thoroughly investigated.[16b,19] Relationships between the types of catalysts and the isomerization rates of unsaturated alcohols to carbonyl compounds are under investigation.

Complex **1a** also catalyses the hydrogenation of the carbonyl group of aldehydes to give alcohols. The results obtained with unsubstituted cinnamaldehyde revealed that hydrogenation of the carbonyl group is much slower than that of the olefinic group (Scheme 2). Saturated aldehydes could be produced *via* direct carbonyl group hydrogenation of $PhCH{=}CRCHO$ or olefinic group hydrogenation $PhCH{=}CRCH_2OH$ followed by isomerization to $PhCH_2CHRCHO$ as observed previously with $[Ir(ClO_4)(CO)(PPh_3)_2]$.[20] In separate experiments $PhCH_2CH_2CHO$ was not detected during the reaction of $PhCH{=}CHCH_2OH$ with **1a** under H_2 ($PhCH_2CH_2CH_2OH$ being the only product). Accordingly, it may be said that $PhCH_2CHRCHO$ are not the isomerization products of $PhCH{=}CRCH_2OH$. The smaller amount of $PhCH_2CH(Me)CHO$ [than $PhCH{=}C(Me)CH_2OH$] observed in the reactions of $PhCH{=}C(Me)CHO$ (Scheme 2) is understood in terms of steric effects of the methyl group which hinders the interaction between the metal and the olefinic group. The fact that $PhCH_2CHClCHO$ and $PhCH_2CHClCH_2OH$ are not detected during the reactions of $PhCH{=}C(Cl)CHO$ could not be explained simply by the steric effects of Cl, but may be understood by the Ir–Cl interaction which somehow interferes with the hydrogenation of the adjacent olefinic group. The compound $PhCH_2CHMe_2$ could be produced by the hydrogenolysis of $PhCH_2CH(Me)CH_2OH$, and/or hydrogenolysis of $PhCH{=}C(Me)CH_2OH$ (to give $PhCH{=}CMe_2$) and subsequent hydrogenation (of $PhCH{=}CMe_2$) as observed with other cationic iridium(I) complexes.[20]

Experimental

Caution: Precautions should be taken in handling perchlorate salts and perchlorato organometallic compounds because they are potentially explosive.

Instruments.—Proton NMR spectra were measured on a Bruker WP 80-MHz FT-NMR spectrometer, infrared and electronic absorption spectra on Shimadzu IR-440 and UV-240 instruments. A Varian 3700 gas chromatograph was used for analysis in catalytic reactions. Elemental analysis was carried out at the Korea Institute of Science and Technology.

Materials.—Standard vacuum-line and Schlenk glassware were used in all preparations. The compound $[IrCl(cod)(PPh_3)]$ was prepared according to the literature method.[21] Nitriles, unsaturated alcohols and unsaturated aldehydes were purchased from Fluka and Aldrich and used without further purification.

Preparation of $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **1a**.—Silver perchlorate (0.038 g, 0.18 mmol) was added to a dichloromethane (5 cm^3) solution of $[IrCl(cod)(PPh_3)]$ (0.11 g, 0.18 mmol) in the presence of one drop of PhCN under N_2 at room temperature and the reaction mixture was stirred for 30 min until a significant amount of white precipitation (AgCl) was seen in a clear red solution. Addition of hexane (10 cm^3) to the red solution after removal of AgCl by filtration resulted in precipitation of red microcrystals which were collected by filtration, washed with hexane and dried *in vacuo*, $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ (90%, 0.13 g) (Found: C, 51.6; H, 4.25; N, 1.85. $C_{33}H_{32}ClIrNO_4P$ requires C, 51.8; H, 4.20; N, 1.85%). Λ_M = 50 S cm^2 mol^{-1} ([Ir] = 2×10^{-5} mol dm^{-3}) in CH_2Cl_2 at 25 °C (*cf.* 53 S cm^2 mol^{-1} for NBu_4ClO_4). IR (Nujol): ν_{max} at 2240w (C≡N, 2225 for free PhCN) and 1100s (br) cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 20 H) and 2.8–1.3 (m, C_8H_{12}, 12 H). Electronic absorption (CH_2Cl_2): λ_{max} 471, 381 and 290 nm.

Compounds **1b**–**1f** were prepared in the same manner as described for **1a**, gave satisfactory elemental analyses and showed molar conductance values close to that of **1a**.

$[Ir(cod)(PPh_3)(PhCH{=}CHCN)]ClO_4$ **1b**. IR (Nujol): ν_{max} at 2225m (C≡N, 2211 for free $PhCH{=}CHCN$), 1599w (C=C, 1620 for free $PhCH{=}CHCN$) and 1100s (br) cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 20 H), 6.79 (d, $-CH{=}CHCN$, 1 H), 6.18 (d, $=CHCN$, 1 H) and 2.8–1.5 (m, C_8H_{12}, 12 H). Electronic absorption (CH_2Cl_2): λ_{max} 473, 387 and 316 nm.

$[Ir(cod)(PPh_3)(CH_2{=}CHCN)]ClO_4$ **1c**. IR (Nujol): ν_{max} at 2262w (C≡N, 2230 for free $CH_2{=}CHCN$), 1592w (C=C, 1609 for free $CH_2{=}CHCN$) and 1100s (br) cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 15 H), 5.8 (m, $CH_2{=}CH$, 3 H) and 2.8–1.5 (m, C_8H_{12}, 12 H). Electronic absorption (CH_2Cl_2): λ_{max} 468, 381 and 318 nm.

$[Ir(cod)(PPh_3)\{CH_2{=}C(Me)CN\}]ClO_4$ **1d**. IR (Nujol): ν_{max} at 2254w [C≡N, 2225 for free $CH_2{=}C(Me)CN$], 1613w [C=C, 1626 for free $CH_2{=}C(Me)CN$] and 1100s (br) cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 15 H), 5.78 (m, $CH_2{=}$, 2 H), 2.8–1.5 (m, C_8H_{12}, 12 H) and 1.67 (s, CH_3, 3 H). Electronic absorption (CH_2Cl_2): λ_{max} 469, 379 and 288 nm.

$[Ir(cod)(PPh_3)(MeCH{=}CHCN)]ClO_4$ **1e**. IR (Nujol): ν_{max} at 2255w (C≡N, 2221 for free $MeCH{=}CHCN$), 1627w (C=C, 1636 for free $MeCH{=}CHCN$) and 1100s (br) cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 15 H),6.8–6.1 ($MeCH{=}CHCN$, 1 H), 5.75 (m, *cis*-$MeCH{=}CHCN$ 0.7 H), 5.63 (m, *trans*-$MeCH{=}CHCN$, 0.3 H), 2.5–1.2 (m, C_8H_{12}) (integrals for CH_3 and C_8H_{12} protons not clearly separated), 1.82 (dd, *trans*-$MeCH{=}CHCN$),[8a] and 1.36 (dd, *cis*-$MeCH{=}CHCN$).[8a] Electronic absorption (CH_2Cl_2): λ_{max} 471, 384 and 317 nm.

$[Ir(cod)(PPh_3)(CH_2{=}CHCH_2CN)]ClO_4$ **1f**. IR (Nujol): ν_{max} at 2287w (C≡N, 2251 for free $CH_2{=}CHCH_2CN$), 1644w (C=C, 1646 for free $CH_2{=}CHCH_2CN$) and 1100s (br) cm^{-1} (ClO_4). ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 15 H), 5.10 (m, $CH_2{=}CH$, 3 H), 5.05, 2.8–1.5 (m, C_8H_{12}, 12 H) and 3.45 (d, CH_2CN, 2 H). Electronic absorption (CH_2Cl_2): λ_{max} 462, 373 and 286 nm.

Preparation of $[IrH_2(cod)(PPh_3)(PhCN)]ClO_4$ **2a**.—An orange solution of compound **1a** (0.1 g, 0.131 mmol) in CH_2Cl_2 (10 cm^3) stirred under atmospheric pressure of H_2 at −78 °C turned pale yellow within 1 h. Addition of cold hexane (20 cm^3, −78 °C) resulted in precipitation of beige microcrystals which were collected by filtration at −78 °C, washed with cold hexane

(20 cm^3) and dried *in vacuo*. Yield 85%. See text for ^1H NMR and IR spectral data and characterization.

Thermal Decomposition of Compound **2a**.—A $CDCl_3$ (1 cm^3) solution of compound **2a** (150 mg, 0.2 mmol) in a round bottom flask (250 cm^3) at −50 °C under N_2 was warmed to 15 °C at which temperature the reaction mixture was kept and ^1H NMR spectral changes were measured at intervals (see Fig. 1). Cyclooctane (*ca.* 20% of **2a**) was separated from the reaction mixture by a solid CO_2–acetone trap and identified at the end of the experiments.

Reaction of $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **1a** *with* PPh_3.—A benzene (20 cm^3) solution of compound **1a** (0.1 g, 0.131 mmol) was heated to reflux in the presence of excess of PPh_3 (0.175 g, 0.66 mmol) for 1 h to give deep red microcrystals which were collected by filtration, washed with benzene (20 cm^3), dried *in vacuo* and identified by ^1H NMR and IR spectroscopy as $[Ir(cod)(PPh_3)_2]ClO_4$.[1d,2e]

Reaction of Compound **1a** *with* CO.—An orange CH_2Cl_2 solution (10 cm^3) of compound **1a** (0.1 g, 0.131 mmol) was stirred under atmospheric pressure of CO at room temperature, turning pale yellow within 10 min. Addition of hexane (20 cm^3) resulted in yellow microscrystals which were collected by filtration, washed with hexane and dried *in vacuo*. IR (Nujol): ν_{max} at 2072s, 2015s (C≡O) and 1100s (br) cm^{-1} (ClO_4); ν(C≡N) of PhCN not observed. ^1H NMR ($CDCl_3$): δ 7.4 (m, C_6H_5, 15 H) 4.15 (m, C_8H_{12}, 4 H) and 2.35 (m, C_8H_{12}, 8 H). Further reaction of **1a** with CO for more than 30 min under the same conditions gave a yellow solid whose ^1H NMR and IR spectra show only signals due to PPh_3 protons (none due to cod) and three ν(C≡O) absorptions at 2010–2080 cm^{-1}.

Catalytic Isomerization of CH_2=$CHCH_2OH$ *with* $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **1a**.—Compound **1a** (77 mg, 0.1 mmol) was added to CH_2=$CHCH_2OH$ (0.5 cm,[3] 7.5 mmol) at room temperature in a NMR tube. The violent exothermic isomerization (to give $MeCH_2CHO$) immediately began to warm the reaction mixture and complete the reaction within 1 h. The reaction was followed by measuring the signals of the product, $MeCH_2CHO$, at δ 9.60 (t, CHO), 2.40 (dq, CH_2) and 1.05 (t, CH_3). To observe a considerable amount of the intermediate enol, MeCH=CHOH, the reaction was initiated at −20 °C in an ice–NaCl bath and the mixture was then removed and placed in another bath maintained at 5–8 °C immediately after initiation of the exothermic isomerization. Repetitive ^1H NMR spectral measurements showed generation of the enol, which slowly undergoes ketonization. Generation of the enol could be followed by measuring the signals due to CH_3 of the *Z* isomer at δ 1.41 (dd) and of the *E* isomer at δ 1.44 (dd).[17a]

Catalytic Isomerization of Unsaturated Alcohols CH_2=$CHCH(Me)OH$ *and* CH_2=$CHCH(Ph)OH$ *with Compounds* **1a** *and* **1c**–**1f**.—These catalytic reactions were carried out in the same manner using the same amounts of catalyst and unsaturated alcohol under the same experimental conditions as described above for the reaction of CH_2=$CHCH_2OH$. Complex **1b** is hardly soluble in these unsaturated alcohols and its catalytic activities in neat alcohols have not yet been investigated. In general, the isomerization of CH_2=CH-$CH(R)OH$ (R = Me or Ph) are faster than that of CH_2=$CHCH_2OH$ with most catalysts and faster with aliphatic nitrile complexes, **1c**–**1f**, than with the aromatic nitrile complex **1a**.

Reaction of cis-$HOCH_2CH$=$CHCH_2OH$ *with* $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **1a**.—Compound **1a** (77 mg, 0.1 mmol) was added to a $CDCl_3$ (0.4 cm^3) solution of *cis*-$HOCH_2CH$=$CHCH_2OH$ (0.25 cm^3, 3 mmol). The resulting solution was stirred under N_2 and ^1H NMR spectra were measured at intervals for 5 h until most of the starting material had disappeared. New signals of $\overline{OCH_2CH_2CH_2CH(OH)}$ at δ 1.89 [m, $CH_2CH_2CH_2CH(OH)$], 3.0–5.0 (s, OH), 3.80 (m, OCH_2CH_2) and 4.92 [m, CH(OH)] gradually increased at the expense of those of *cis*-$HOCH_2CH$=$CHCH_2OH$ at δ 4.13 (d, CH_2), 4.0–6.0 (s, OH) and 5.62 (t, CH=CH). A small triplet at δ 9.50 appeared and disappeared several times during the 5 h reaction. The position, multiplicity and small coupling constant (*ca.* 2 Hz) unambiguously identify it as due to CH_2CHO (probably of $HOCH_2CH_2CH_2CHO$, the double-bond migration product of *cis*-$HOCH_2CH$=$CHCH_2OH$).

Catalytic Hydrogenation of Unsaturated Aldehydes, PhCH=CRCHO (R = H, Me *or* Cl) *with Compound* **1a**.—Compound **1a** (0.1 mmol, 77 mg) and PhCH=CRCHO (15 mmol) were added to $CDCl_3$ (2.0 cm^3) under hydrogen in a bomb-type reactor (Parr 1341, volume 360 cm^3) into which hydrogen was introduced until the pressure reached 6 atm at 25 °C. The reactor was then placed in an oven maintained at 50 °C for 3 h and cooled on an ice-bath before it was opened for analysis of the reactant and products. Analysis was carried out mostly by ^1H NMR spectral measurements and in some cases by GC with coinjection of authentic samples. Proton NMR signals (in $CDCl_3$) employed for analysis were as follows: PhCH=CHCHO, δ 9.70 (d); $PhCH$=$CHCH_2OH$, δ 4.25 (br d); $PhCH_2CH_2CHO$, δ 2.5–3.0 (m); $PhCH_2CH_2CH_2OH$, δ 3.60 (t), 2.60 and 1.80 (m); PhCH=C(Me)CHO, δ 9.55 (s); $PhCH$=$C(Me)CH_2OH$, δ 4.21 (s); $PhCH_2CH(Me)CHO$, δ 3.00 (m); $PhCH_2CH(Me)CH_2OH$, δ 3.45 (d); PhCH=C(Cl)CHO, δ 9.35 (s); $PhCH$=$C(Cl)CH_2OH$, δ 4.30 (s); $PhCH_2CH(Cl)CHO$, δ 3.61 (m); $PhCH_2CH(Cl)$-CH_2OH, δ 3.33 (d).

Catalytic Reaction of $PhCH$=$CHCH_2OH$ *with Compound* **1a**.—This reaction was carried out at 25 °C under p_{H_2} = 6 atm for 2 h using compound **1a** (0.1 mmol, 77 mg) and $PhCH$=$CHCH_2OH$ (3.0 mmol, 420 mg) in $CDCl_3$ (2.0 cm^3) in the same manner as described above for the hydrogenation of PhCH=CRCHO. A part (*ca.* 0.5 cm^3) of the reaction mixture was taken out of the reactor at intervals and analysed by ^1H NMR measurements. No isomerization product, $PhCH_2CH_2$-CHO, was detected during the reaction. Almost all of $PhCH$=$CHCH_2OH$ was hydrogenated to give $PhCH_2CH_2$-CH_2OH within 2 h.

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