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Synthesis, Reactions and Catalytic Activities of Iridium Complexes intercalated into Montmorillonite

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Reactions of cationic iridium(I) complexes, $[Ir(cod)(PPh_3)_2]ClO_4$ **1** and $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **2** (cod = cycloocta-1,5-diene) with water-swelled sodium montmorillonite have been shown to produce iridium complex-intercalated clays, $[Ir(cod)(PPh_3)_2]^+$–montmorillonite **1c** and $[Ir(cod)(PPh_3)(PhCN)]^+$–montmorillonite **2c**. Compounds **1c** and **2c** react with CO to produce $[Ir(CO)_x(PPh_3)_2]^+$ (from **1c**) and $[Ir(CO)_y(PPh_3)]^+$(from **2c**) intercalated clays. Reactions of **1c** and **2c** with H_2 produce cyclooctane and unknown iridium complexes remaining in the layers of the clay. While both the catalytic hydrogenation and isomerization (double-bond migration and *cis–trans* conversion) of olefins with **1** and **2** are in general retarded by intercalation of the catalysts, isomerization is relatively more suppressed than hydrogenation. Selective hydrogenation of the vinyl group of 4-vinylcyclohexene was found to be somewhat higher with **1c** than with **1**.

In the search for methods of improving selectivities in transition-metal-catalysed reactions, transition-metal complex-intercalated clays have been prepared and their catalytic activities investigated.[1–12] Several studies have been made of rhodium complexes intercalated into the layers of smectite clays,[7–12] while there has been, to our knowledge, only one report on iridium complex–clay intercalation.[6] We now report the intercalation of the complexes $[Ir(cod)(PPh_3)_2]^+$ and $[Ir(cod)(PPh_3)(PhCN)]^+$ (cod = cycloocta-1,5-diene) into layers of montmorillonite together with their reactions with CO and H_2 and catalytic characteristics for hydrogenation and isomerization of olefinic groups. Montmorillonite-supported $[Ir(cod)(PPh_3)_2]^+$ and its reactions and catalytic activities is reported for comparison.

Experimental

Materials.—Sodium montmorillonite (Creek County, Wyoming, USA) was obtained from the Source Clay Mineral Repository, Clary Minerals Society. Elemental analysis (SiO_2, 55.6; Al_2O_3, 20.1; Fe_2O_3, 3.7; Na_2O, 2.8; MgO, 2.5; K_2O, 0.6; CaO, 0.5%) shows the cation-exchange capacity to be 121 milliequivalents of cation (M^+) per 100 g of this clay. The complexes $[Ir(cod)(PPh_3)_2]ClO_4$ **1**, $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **2** and $[Ir(cod)(PhCN)_2]ClO_4$ **3** were prepared by the literature methods.[13–15] Organic substrates, hex-1-ene, cod, 4-vinylcyclohexene, diphenylacetylene and but-3-en-2-ol from either Fluka or Aldrich were used as purchased.

Instrumentation.—Proton NMR, IR and electronic absorption and diffuse reflectance spectra were recorded on Varian EM-360A (at 60 MHz), Shimadzu IR-400 and UV-240 spectrophotometers, respectively. Electronic diffuse reflectance spectra of solid samples were obtained in alumina using a 204-52454 integrating sphere attachment. X-Ray diffraction (XRD) data were obtained on a Rigaku RAD-C diffractometer with nickel-filtered Cu-Kα radiation and calibration with a silicon polycrystal as a standard. A Varian 3700 gas chromatograph with a column (4.8 m × 0.32 mm) of 5% KOH on Carbowax 20M was used for analysis of the reaction mixtures.

Synthesis.—Swelling of sodium montmorollonite. Sodium montmorillonite (45 mg) was slowly added to distilled water (5 cm^3) and the resulting mixture was stirred under N_2 for 30 min. It was used *in situ* for intercalation of the iridium complex without separation of the water-swelled clay and excess of water. For XRD measurements, the swelled montmorillonite was filtered off and dried under N_2 at room temperature for 1 h.

$[Ir(cod)(PPh_3)_2]^+$*–montmorillonite* **1c**. A red solution of $[Ir(cod)(PPh_3)_2]ClO_4$ (0.1 mmol, 93 mg) in methanol (30 cm^3) was slowly added to the beige slurry of swelled montmorillonite (45 mg of clay in 5 cm^3 of water) prepared as described above and the resulting mixture was stirred for 3 h under N_2 at room temperature. The reddish iridium-intercalated montmorillonite was then filtered off, washed with MeOH on a fritted glass filter (medium porosity) until the filtrate became colourless, and used in catalytic reactions without thorough drying. The sample was dried under N_2 at room temperature for 1 h for XRD analysis.

$[Ir(cod)(PPh_3)(PhCN)]^+$*–montmorillonite* **2c**. This orange material (**2** is also orange) was prepared in the manner described for $[Ir(cod)(PPh_3)_2]^+$–montmorillonite **1c**.

Attempt to prepare $[Ir(cod)(PhCN)_2]^+$*–montmorillonite.* To the slurry of swelled montmorillonite (45 mg of clay in 5 cm^3 water) was added a yellow solution of $[Ir(cod)(PhCN)_2]ClO_4$ (0.1 mmol) in MeOH (30 cm^3) and the resulting mixture was stirred under N_2 at room temperature for 3 h. The yellow solid was filtered off, washed with MeOH on a fritted glass filter until the filtrate became colourless and dried under N_2 at room temperature for 1 h for XRD analysis.

Stoichiometry of the intercalation of $[Ir(cod)(PPh_3)_2]^+$. A methanol solution (25 cm^3) containing $[Ir(cod)(PPh_3)_2]ClO_4$ (0.04 mmol) was mixed with a slurry of montmorillonite (20 mg) swelled with water (5 cm^3) and stirred for 3 h under nitrogen at room temperature. The absorbance of the supernatant was measured as 0.270 (in a 1 cm path length cell) at 491 nm {see Fig. 1 for the electronic absorption spectrum of $[Ir(cod)(PPh_3)_2]ClO_4$} while the absorbance of a methanol (25 cm^3)–water (5 cm^3) solution containing $[Ir(cod)(PPh_3)_2]ClO_4$ (0.04 mmol) at 491 nm was found to be 0.373. These data suggest that 1 mmol of $[Ir(cod)(PPh_3)_2]ClO_4$ reacts with *ca.* 1.8 g of sodium montmorillonite to give $[Ir(cod)(PPh_3)_2]^+$–montmorillonite **1c** containing *ca.* 0.55 mmol Ir per gram of clay.

$[Ir(cod)(PPh_3)_2]^+$ *adsorbed on montmorillonite* **1s**. This compound was prepared in a similar manner to that of **1c** except

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that water was never used since **1c** is obtained only when water is used (see below).

Stoichiometry of the adsorption of $[Ir(cod)(PPh_3)_2]^+$ *by montmorillonite.* The stoichiometry, 1 mmol of $[Ir(cod)(PPh_3)_2]^+$ to *ca.* 5.2 g of clay, was determined by measuring the difference between the absorbances of $[Ir(cod)(PPh_3)_2]^+$ at 491 nm before and after addition of the clay as described above for the stoichiometry of the intercalation. A similar value, 1 mmol of Ir^+ to *ca.* 5.5 g clay, was also obtained by gravimetric analysis carried out by measuring the difference between the weights of sodium montmorillonite and montmorillonite-supported $[Ir(cod)(PPh_3)_2]^+$ **1s**. The air-dried sodium montmorillonite used in this study may contain a small amount of water, and a small amount of **1c** may be formed during the measurements.

Reactions.—$[Ir(cod)(PPh_3)_2]^+$*–montmorillonite* **1c** *with* CO. A suspension of compound **1c** (120 mg) in $CHCl_3$ (10 cm^3) was stirred under atmospheric pressure of CO at room temperature for 10 h. The initially reddish suspension turned white within 10 min. A white solid was filtered off and washed thoroughly with $CHCl_3$. The ^1H NMR spectrum of the less-volatile material obtained by evaporating the filtrate showed signals due to cycloocta-1,5-diene.

$[Ir(cod)(PPh_3)(PhCN)]^+$*–montmorillonite* **2c** *and* $[Ir(cod)(PhCN)_n]^+$*–montmorillonite* **3c** *with* CO. These reactions were carried out in the same manner as described above. The orange **2c** turned white while yellow **3c** turned dark brown. Proton NMR and gas chromatographic analysis showed cod and PhCN in the filtrates. Only a small amount of PhCN was found in the filtrate from the reaction of **3c**.

Compound **1c** *with* H_2. A suspension of compound **1c** (66 mg) in $CDCl_3$ (5 cm^3) was stirred under atmospheric pressure of H_2 at room temperature for 10 h. The reddish suspension turned white within 5 min and then dark grey within 3 h. The supernatant obtained upon centrifugation was found to contain cyclooctane according to ^1H NMR and GC analysis.

Compounds **2c** *and* **3c** *with* H_2. These reactions were carried out in the same manner as described above. Proton NMR and GC analysis showed cyclooctane and PhCN to be present in the supernatants.

Compound **1c** *with* $NaClO_4$. Sodium perchlorate (0.1 g, 0.8 mmol) in water (5 cm^3) was added to the slurry of compound **1c** [145 mg containing 0.055 mmol (45 mg) of the iridium complex] in a mixture of MeOH (20 cm^3) and CH_2Cl_2 (10 cm^3) and the resulting mixture was stirred for 15 h under N_2 at room temperature. The filtrate obtained using a medium-porosity fritted glass filter was extracted several times with water to remove the unreacted $NaClO_4$ and evaporated under vacuum to obtain a small amount (*ca.* 5 mg) of red solid identified as $[Ir(cod)(PPh_3)_2]ClO_4$ **1** by ^1H NMR, infrared and visible-region electronic absorption spectra.

Catalytic Hydrogenations.—With $[Ir(cod)(PPh_3)_2]$*–montmorillonite* **1c**. Compound **1c** (66 mg) containing $[Ir(cod)(PPh_3)_2]^+$ (0.025 mmol) and hex-1-ene (2.5 mmol) in $CDCl_3$ (5 cm^3) were stirred under atmospheric pressure of H_2 at 25 °C. A part (*ca.* 0.5 cm^3) of the mixture was taken out of the reactor at intervals and the supernatant obtained by centrifugation was analysed by ^1H NMR spectroscopy. Disappearance of the starting material hex-1-ene could readily be followed by the disappearance of the multiplets at δ 5.70 and 4.90. The isomerization product hex-2-ene was measured by the multiplet at δ 5.40. Hydrogenation of both hex-1-ene and -2-ene to produce hexane could be followed by the disappearance of the multiplets at δ 5.70 and 4.90 of hex-1-ene and δ 5.40 of hex-2-ene and also by the disappearance of the multiplet at δ 2.0 for both hex-1-ene and -2-ene.

With montmorillonite-supported $[Ir(cod)(PPh_3)_2]^+$ **1s** *and with swelled sodium montmorillonite.* These reactions were carried out in the same manner.

With $[Ir(cod)(PPh_3)_2]ClO_4$ **1**. These homogeneous catalytic reactions were carried out in the manner described for **1c**. Separation of soluble catalysts was not necessary for the product analysis by ^1H NMR spectroscopy unless the signals due to the catalysts interfered.

*Isomerization of But-*3*-en-*2*-ol with Compounds* **1**, **1c**, **2** *and* **2c**.—These experiments were carried out in the manner described above for the hydrogenation with **1c** except that they were carried out under N_2 (in the absence of H_2). The disappearance of but-3-en-2-ol was followed by the disappearance of the signals at δ 4.0–6.0 due to the olefinic protons, and the formation of ethyl methyl ketone was followed by the appearance of the signal at δ 2.12 due to $COCH_3$.

Results and Discussion

Reactions of $[Ir(cod)(PPh_3)_2]ClO_4$ **1** and $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **2** with sodium montmorillonite swelled with water produced the intercalated iridium compounds $[Ir(cod)(PPh_3)_2]^+$–montmorillonite **1c** and $[Ir(cod)(PPh_3)(PhCN)]^+$–montmorillonite **2c** through cation exchange between the Na^+ of the clay and $[Ir(cod)L_2]^+$ [$L_2 = (PPh_3)_2$ or $(PPh_3)(PhCN)$], see equation (1). A rhodium analogue $[Rh(cod)(PPh_3)_2]^+$–hectorite was previously reported.[7] Attempts to prepare $[Ir(cod)(PhCN)_2]^+$–montmorillonite have also been carried out by the reaction of $[Ir(cod)(PhCN)_2]ClO_4$ **3** with the swelled sodium montmorillonite. The yellow solid isolated, however, does not seem to contain intact $[Ir(cod)(PhCN)_2]^+$ (see below). According to the X-ray diffraction data, the intercalation of iridium complexes **1** and **2** into layers of sodium montmorillonite does not occur in the absence of water and samples are best prepared from the reaction of iridium complexes with water-swelled clay. Expansion of interlayer distances by swelling with water may facilitate intercalation of the iridium complexes. In MeOH or CH_2Cl_2 in the absence of water, however, significant amounts of **1**–**3** seem to be adsorbed on the surfaces of the clay.

$$\underline{\overline{Na^+(H_2O)}} + [Ir(cod)L_2]^+ \longrightarrow \underline{\overline{[Ir(cod)L_2]^+(H_2O)}} + Na^+ \quad (1)$$

Characterization of Iridium Complexes intercalated into Montmorillonite.—Stoichiometry. The observed ratio, Ir (in mmol):sodium montmorillonite (in g), of *ca.* 0.55:1 for the intercalation compound **1c** (see Experimental section) corresponds to *ca.* 46% of the cation-exchange capacity (*ca.* 120 milliequivalents of M^+ per 100 g) of the clay being replaced by Ir^+. Elemental analysis (C, 16.75%) gives a similar ratio 0.51:1. The fact that the montmorillonite-supported compound **1s** (for which no expansion of the basal spacing was observed) contains *ca.* 0.19 mmol of the iridium complex per gram of clay suggests that *ca.* 19/55 of the iridium complex in **1c** is adsorbed (not intercalated) on the edge of the clay. A cation-exchange limit of *ca.* 22% was reported for $[Rh(cod)(PPh_3)_2]^+$–hectorite[7] with a basal spacing of 17.7 Å which allows only monolayer intercalation, while 100 and 160% of the cation-exchange capacity of sodium–montmorillonite were found to be replaced by Λ-$[Ru(phen)_3]^{2+}$ and *rac*-$[Ru(phen)_3]^{2+}$ (phen = 1,10-phenanthroline) with basal spacings expanded up to 17.8 and 29.7 Å, respectively.[3]

Electronic Spectra.—Electronic diffuse reflectance spectra of compounds **1c** and **2c** show three bands at practically the same wavelengths as those of **1** and **2** (see Fig. 1), which suggests intact $Ir(cod)(PPh_3)_2$ and $Ir(cod)(PPh_3)(PhCN)$ moieties in **1c** and **2c**, respectively. The spectrum of **3c** (the reaction product of **3** with water-swelled sodium montmorillonite) does not show a

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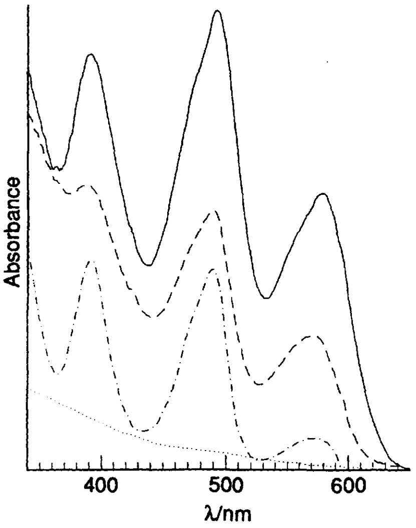

Fig. 1 Electronic diffuse reflectance spectra of $[Ir(cod)(PPh_3)_2]ClO_4$ **1** (——), $[Ir(cod)(PPh_3)_2]^+$-montmorillonite **1c** (– – – –), sodium montmorillonite (· · · ·) in alumina and the absorption spectrum of **1** (— · — · —) in methanol. Different concentrations were chosen for each sample for clarity

Table 1 Basal spacings (001) of iridium complexes intercalated in montmorillonite

Compound	001 spacing[a]/Å
Sodium montmorillonite	9.4
Sodium montmorillonite–water[b]	12.9
$[Ir(cod)(PPh_3)_2]^+$-montmorillonite **1c**	24.9
$[Ir(CO)_x(PPh_3)_2]^+$-montmorillonite[c]	22.3
$[Ir(PPh_3)_2]^+$-montmorillonite[d]	18.2
$[Ir(cod)(PPh_3)(PhCN)]^+$-montmorillonite **2c**	21.5
$[Ir(CO)_y(PPh_3)]^+$-montmorillonite[e]	20.7
$[Ir(cod)(PhCN)_n]^+$-montmorillonite **3c**[f]	18.2
$[Ir(CO)_z]^+$-montmorillonite[g]	17.1

[a] Average values of several samples. [b] Sodium montmorillonite swelled with water. [c] The reaction product of compound **1c** with CO. [d] The reaction product of compound **1c** with H_2. [e] The reaction product of compound **2c** with CO. [f] The isolated solid from the reaction of $[Ir(cod)(PhCN)_2]ClO_4$ **3** with sodium montmorillonite (see text for characterization). [g] The reaction product of compound **3c** with CO.

band in the visible region while **3** shows three bands at 369, 442 and 496 nm in CH_2Cl_2. This indicates that the $Ir(cod)(PhCN)_2$ moiety is not maintained during cation exchange between **3** and sodium montmorillonite. It should be mentioned, however, that cod and PhCN were found in the reaction mixture of **3c** with CO and H_2 (see reactions below and Experimental section).

X-Ray Diffraction Data.—The X-ray diffraction data in Table 1 unambiguously demonstrate intercalation of the iridium complexes into the clay. The basal spacings of 24.9 and 21.5 Å observed for **1c** and **2c** are very close to the sums (24.9 and 22.4 Å) of those for water-swelled sodium montmorillonite (12.9 Å) and the molecular models of $[Ir(cod)(PPh_3)_2]^+$ (12.0 Å) and $[Ir(cod)(PPh_3)(PhCN)]^+$ (9.5 Å), respectively. The basal spacing (18.2 Å) observed for **3c** (the product of the reaction of **3** with sodium montmorillonite) is also close to the sum (17.9 Å) of 12.9 and 5.0 Å {from the molecular model of $[Ir(cod)(PhCN)_2]^+$}. Although the XRD data for **3c** suggest intercalation of an iridium complex into the clay, the electronic absorption spectrum is not consistent with a $Ir(cod)(PhCN)_2$ moiety. Therefore **3c** is denoted by $[Ir(cod)(PhCN)_n]^+$-montmorillonite since **3c** seems to contain both cod and PhCN (see reactions with CO in Experimental section).

The interlayer distance (24.9 Å) observed for compound **1c** is certainly larger than that (17.7 Å) observed for the rhodium analogue $[Rh(cod)(PPh_3)_2]^+$-hectorite prepared in acetone.[7] Reactions with CO cause slight decreases in the basal spacings of **2c** and **3c** (see Table 1), which may be understood as replacement of cod and PhCN with CO as observed (see Experimental section). The relatively large decrease (2.6 Å) observed for the product of the reaction of **1c** with CO may be understood in terms of replacement of cod with CO and rearrangement of the two PPh_3, possibly from *cis* (in **1c**) to *trans* {in $[Ir(CO)_x(PPh_3)_2]^+$-montmorillonite} to each other. The larger decrease in basal spacing observed for the product of the reaction of **1c** with H_2 (see Table 1) may be explained by desorption of cod probably immediately after its hydrogenation to cyclooctane. It might be safely said that the reactions of **1c**, **2c** and **3c** with CO and H_2 do not cause desorption of iridium from the layers of the clay.

Reactions.—*With* CO. The iridium complex-intercalated montmorillonites **1c**–**3c** react with CO to give Ir–CO complexes which are still in between the layers of the clay according to the X-ray diffraction data in Table 1. The products obtained show strong absorption bands due to terminal CO at 1991 and 1993 (white solid from **1c**), 2047 and 1994 (white solid from **2c**) and 2055 cm^{-1} (somewhat broad) (dark brown solid from **3c**) in Nujol. As mentioned above, cod and PhCN in **1c**–**3c** are replaced by CO [equations (2)–(4)]. We have found that the

$$\underset{\textbf{1c}}{\underline{\overline{[Ir(cod)(PPh_3)_2]^+}}} \xrightarrow[-\mathrm{cod}]{x\mathrm{CO}} \underline{\overline{[Ir(CO)_x(PPh_3)_2]^+}} \qquad (2)$$

$$\underset{\textbf{2c}}{\underline{\overline{[Ir(cod)(PPh_3)(PhCN)]^+}}} \xrightarrow[-\mathrm{cod},\ -\mathrm{PhCN}]{y\mathrm{CO}} \underline{\overline{[Ir(CO)_y(PPh_3)]^+}} \qquad (3)$$

$$\underline{\overline{[Ir(cod)(PhCN)_n]^+}} \xrightarrow[-n\mathrm{PhCN},\ -\mathrm{cod}]{z\mathrm{CO}} \underline{\overline{[Ir(CO)_z]^+}} \qquad (4)$$

replacement of cod and PhCN with CO (probably more than one CO) readily occurs also for the non-intercalated compounds **1**–**3**,[13,16] and it has been known that cod coordinated to iridium(I) is readily replaced by CO.[17]

We also found that the reaction of non-intercalated iridium complex **1** with CO in solution produces a white solid $[Ir(CO)_3(PPh_3)_2]ClO_4$[18] which reacts further with water-swelled sodium montmorillonite to give a white solid which showed infrared bands at 1991 and 1993 cm^{-1}.

It has been found that reactions of compounds **1c** and **2c** with CO liberate small amounts of PPh_3 and the desorption of PPh_3 became significant at longer reaction times with slight shifts of ν(CO).

With H_2. Reactions of iridium–clay compounds **1c**–**3c** with H_2 produce cyclooctane [equations (5) (L = PPh_3 or PhCN) and (6)]. The isolated products do not show infrared bands

$$\underline{\overline{[Ir(cod)(PPh_3)L]^+}} \xrightarrow{H_2} C_8H_{16} + \text{unknown iridium compound} \qquad (5)$$

$$\underline{\overline{[Ir(cod)(PhCN)_n]^+}} \xrightarrow{H_2} C_8H_{16} + \text{iridium powder} + n\mathrm{PhCN} \qquad (6)$$

attributable to ν(Ir–H). The products from the reactions of **1c** and **2c** show bands due to Ir–PPh_3 [equation (5)] and a basal spacing of 18.2 Å was found for the product of reaction of **1c**. On the other hand, the product from the reaction of **3c** shows only the infrared bands of the clay. This reaction produces metallic

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Table 2 Catalytic hydrogenation and isomerization of olefins with $[Ir(cod)(PPh_3)_2]ClO_4$ **1**, $[Ir(cod)(PPh_3)_2]^+$–montmorillonite **1c**, $[Ir(cod)(PPh_3)(PhCN)]ClO_4$ **2** and $[Ir(cod)(PPh_3)(PhCN)]^+$–montmorillonite **2c**, under an atmospheric pressure of H_2 at 25 °C in $CDCl_3$. Mole ratios of substrates to Ir were 200 for 4-vinylcyclohexene, 100 for hex-1-ene and but-3-en-2-ol, 50 for cod and 20 for diphenylacetylene using 0.025 mmol of Ir

Catalyst	Substrate	*t*/h	Product (%)
Clay[a]	Hex-1-ene	1	Hexane (15), no hex-2-ene
1c		1	Hexane (37), hex-2-ene (63)
		7	Hexane (100)
1s[b]		1	Hexane (13), hex-2-ene (54)
1		0.2	Hexane (23), hex-2-ene (77)
		1	Hexane (100)
2c		1	Hexane (9), hex-2-ene (41)
		7	Hexane (63), hex-2-ene (37)
2		1.5	Hexane (100)
Clay[a]	cod	24	No hydrogenation
1c		2	Cyclooctene (58)
		4	Cyclooctane (100)
1		1	Cyclooctene (42)
		2	Cyclooctane (100)
Clay[a]	4-Vinylcyclohexene	24	No hydrogenation
1c		3	4-Ethylcyclohexene (44)
		5	4-Ethylcyclohexene (64), Ethylcyclohexane (13)
1		3	4-Ethylcyclohexene (40), ethylcyclohexane (15)
		5	4-Ethylcyclohexene (41), ethylcyclohexane (59)
2c		5	4-Ethylcyclohexene (32)
2		3	4-Ethylcyclohexene (30), ethylcyclohexane (5)
Clay[a]	Diphenylacetylene	24	No hydrogenation
1c		2.5	*cis*-1,2-Diphenylethylene (100)
		5.5	*cis*-1,2-Diphenylethylene (72), *trans*-1,2-diphenylethylene (17), 1,2-diphenylethane (11)
1		0.5	*cis*-1,2-Diphenylethylene (100)
		1	*cis*-1,2-Diphenylethylene (13), *trans*-1,2-diphenylethylene (73), 1,2-diphenylethane (14)
Clay[a]	But-3-en-2-ol	24	No reaction
1c		5	Ethyl methyl ketone (7)
1		5	Ethyl methyl ketone[c] (65)
2c		4	Ethyl methyl ketone[c] (85)
2		0.1	Ethyl methyl ketone (100)

[a] A water-swelled sodium montmorillonite (45 mg) which could contain 0.025 mmol of $[Ir(cod)(PPh_3)_2]^+$. [b] Montmorillonite-supported $[Ir(cod)(PPh_3)_2]^+$ {151 mg which was found to contain 0.025 mmol of $[Ir(cod)(PPh_3)_2]^+$}. [c] Isomerisation is much faster under H_2 than under N_2. Hydrogenation of the carbonyl group of the ketone occurs very slowly.

iridium powders [equation (6)], as does the reaction of **3** with H_2.[16] Metallic powders have been produced from the reactions of M–cod (M = Ir[18] or Pt[19]) complexes with H_2.

$[Ir(cod)(PPh_3)_2]^+$*–montmorillonite* **1c** *with* $NaClO_4$. A small amount of compound **1** was obtained from the reaction of **1c** with excess of $NaClO_4$ (see Experimental section), which suggests that the desorption of $[Ir(cod)(PPh_3)_2]^+$ from **1c** is much less favoured in the equilibrium (7).

$$\underset{\mathbf{1c}}{\underline{\overline{[Ir(cod)(PPh_3)_2]^+}}} + NaClO_4 \rightleftharpoons \underline{\overline{Na^+}} + \underset{\mathbf{1}}{[Ir(cod)(PPh_3)_2]ClO_4} \quad (7)$$

Catalysis.—The water-swelled sodium montmorillonite catalyses the hydrogenation of hex-1-ene, but it is not active for hydrogenation or isomerization of the other unsaturated compounds in Table 2 under our experimental conditions. The catalytic hydrogenation and isomerization of olefins is, in general, considerably slower with **1c** and **2c** than with the soluble non-clay compounds **1** and **2** (see Table 2). The hydrogenation with iridium intercalated into the clay, **1c**, seems somewhat faster than that with the iridium supported on the clay, **1s**. Significant decreases in olefin hydrogenation rates were reported with $Rh(PPh_3)_n^+$ between layers of hectorite.[10] The hydrogenation of hex-1-ene and cycloocta-1,5-diene with **3c** was found to be rapid, which should be understood in terms of the heterogeneous catalysis by iridium metal powders since the reaction of **3c** with H_2 rapidly produces metallic powders of iridium [see equation (6)].

Intercalation of $[Ir(cod)(PPh_3)_2]^+$ into the clay seems to depress more effectively the isomerization of hex-1-ene to -2-ene: the product ratio, hex-2-ene: hexane for the isomerization and hydrogenation of hex-1-ene is higher with compound **1** (3.3 : 1) than that with **1c** (1.7 : 1). A similar effect was prominent with $[Rh(PPh_3)_n]^+$ in hectorite.[10]

Selective hydrogenation of the vinyl group of 4-vinylcyclohexene could be obtained to some extent by employing compounds **1c** and **2c** as catalysts: 4-ethylcyclohexene was the only product up to 44 and 32% of 4-vinylcyclohexene being hydrogenated with **1c** and **2c**, respectively, while a significant amount of ethylcyclohexane was always present in the reaction mixtures when **1** and **2** were used as catalysts (see Table 2).

Intercalation of $[Ir(cod)(PPh_3)_2]^+$ into the clay seems to retard the *cis*/*trans* isomerization more effectively than the hydrogenation of 1,2-diphenylethylene. Both compounds **1** and **1c** catalyse the hydrogenation of diphenylacetylene to give the initial product *cis*-1,2-diphenylethylene which is isomerized to *trans*-1,2-diphenylethylene and hydrogenated to 1,2-diphenylethane. The ratio of *cis*- to *trans*-1,2-diphenylethylene in the reaction mixtures is considerably higher with **1c** (4.2 : 1) than with **1** (0.2 : 1) while about the same amounts (11% with **1c** and 14% with **1**) of 1,2-diphenylethane are produced (see Table 2).

Intercalation into the clay also suppresses the catalytic activities of the iridium complexes **1** and **2** for the isomerization of an unsaturated alcohol, but-3-en-2-ol, to give ethyl methyl ketone (see Table 2).

Finally it should be mentioned that compounds **1c** and **2c** released a small amount of PPh_3 and PhCN when they were stirred under the conditions for catalytic hydrogenation for more than 24 h.

Acknowledgements

We thank the Korea Science and Engineering Foundation for financial support and Lucky R & D Center for elemental analysis and X-ray diffraction measurements.

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Received 7th September 1992; *Paper* 2/04804C

Published on 01 January 1993. Downloaded by Universidade Federal do Parana on 28/07/2013 16:48:14.