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METAL COMPLEXES OF CYANOCARBONS
XII*. HYDRIDO-π-OLEFINIC COMPLEXES OF IRIDIUM

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SUMMARY

Reactions of various activated olefins with $IrH(CO)(PPh_3)_3$, $IrH(CO)_2(PPh_3)_2$, and $IrH_3(CO)(EPh_3)_2$ ($E = P$, As) have been studied, and the complexes IrH(CO)(activated olefin)$(EPh_3)_2$ ($E = P$, activated olefin = fumaronitrile, cinnamonitrile, benzylidenemalononitrile, dimethyl fumarate, and fumaric acid; $E = As$, activated olefin = fumaronitrile) have been isolated and characterized. Several of the analogous deuterio complexes were also prepared, and infrared and NMR studies have yielded information about the structures in both the solid state and in solution. The unsaturated acids, maleic, cinnamic, and fumaric acids protonate the iridium substrates to give the $[IrH_2(CO)(PPh_3)_3]^+$ and $[IrH_2(CO)_2(PPh_3)_2]^+$ cations. The relevance of hydrido-π-olefinic complexes to homogeneous catalysis is discussed, and the catalytic isomerization of dimethyl maleate to dimethyl fumarate by $IrH(CO)(PPh_3)_3$ is reported.

INTRODUCTION

Even though hydrido-π-olefinic complexes of transitional metals are often cited as being probable intermediates in homogeneous catalytic reactions, only a few such compounds have been isolated[2–8], and the presence of an M–H bond in some of these was not verified by preparation of the analogous deuterio complex or measurement of the high field NMR spectrum. The purpose of this work was to prepare some hydrido-π-olefinic complexes so that they could be scrutinized with respect to their possible role in the homogeneous catalytic process. Reported herein are the preparation and characterization of complexes of the type IrH(CO)(activated olefin)$(PPh_3)_2$. A preliminary report of this work has been made[9]. Also, the crystal structure of one of these complexes, IrH(CO)(fumaronitrile)$(PPh_3)_2$, was described[10].

EXPERIMENTAL

I. Materials

The olefins were obtained from commercial sources and were used without further purification. Prepared according to literature procedures, or minor modifi-

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* For Part XI see ref. 1.

cations of these, were $IrH(CO)(PPh_3)_3$[11], $IrH_3(CO)(PPh_3)_2$[12], and $IrH(CO)_2(PPh_3)_2$[13]. The latter compound was also prepared *in situ* by bubbling carbon monoxide through a solution of $IrH_3(CO)(PPh_3)_2$ or $IrH_3(PPh_3)_2$[12].

All reactions were carried out in a nitrogen atmosphere, but work-up of reaction mixtures was usually done in air.

II. Preparation

The preparation of these compounds was straightforward. Generally, the iridium substrate $IrH(CO)(PPh_3)_3$, $IrH(CO)_2(PPh_3)_2$, or $IrH_3(CO)(EPh_3)_2$ (E=P, As), was dissolved in a small volume of solvent (benzene or dichloromethane) in the temperature range 25–75°, an excess of the olefin was added, and the mixture was stirred until precipitation occurred. The solid was collected on a filter, washed with alcohol, recrystallized from a suitable solvent mixture, and dried in a vacuum desiccator. Specific details are given below. IR and NMR spectral data are listed in Tables 1 and 2 respectively.

A. Hydridocarbonyl(fumaronitrile)bis(triphenylphosphine)iridium, $IrH(CO)(NCCH{=}CHCN)(PPh_3)_2$. To a bright yellow solution of $IrH(CO)(PPh_3)_3$ (0.5 g, 0.5 mmoles) in 10 ml of benzene at 50° was added fumaronitrile (0.39 g, 5 mmoles) and the yellow color disappeared to give a clear, colorless solution. After a few minutes a white solid formed. Stirring was continued for $\frac{1}{2}$ h, the solid was collected on a filter, and then washed with methanol, yield 0.4 g (98%) of complex, m.p. 232–235° (dec). Recrystallization from $CHCl_3$/hexane or CH_2Cl_2/methanol gave colorless needles. (Found: C, 59.39; H, 4.23; N, 3.31; P, 7.53; mol. wt. osmometric in $CHCl_3$, 708. $C_{41}H_{33}N_2OP_2Ir$ calcd.: C, 59.77; H, 4.04; N, 3.40; P, 7.52%; mol. wt., 824). The analogous complex deuteriocarbonyl(fumaronitrile)bis(triphenylphosphine)iridium, $IrD(CO)(NCCH{=}CHCN)(PPh_3)_2$, was obtained in a like manner from $IrD(CO)(PPh_3)_3$.

In a second method of preparation $IrH_3(CO)(PPh_3)_2$ (0.37 g, 0.5 mmoles) was added to 10 ml of benzene containing 0.39 g (5 mmoles) of fumaronitrile and the solution was stirred at 25°. No gas evolution was observed initially so the solution was warmed to 40–50° whereupon small bubbles appeared and in $\frac{1}{2}$ h a white solid had precipitated. The solid was collected (0.22 g, 55%) and was shown by an infrared spectrum to be identical to the product obtained from $IrH(CO)(PPh_3)_3$.

The same complex $IrH(CO)(NCCH{=}CHCN)(PPh_3)_2$ was also obtained from the addition of fumaronitrile at 25° to an *in situ* preparation of $IrH(CO)_2(PPh_3)_2$, which was obtained by bubbling carbon monoxide through a benzene solution of $IrH_3(PPh_3)_2$.

B. Hydridocarbonyl(fumaronitrile)bis(triphenylarsine)iridium, $IrH(CO)(NCCH{=}CHCN)(AsPh_3)_2$. Fumaronitrile (0.24 g, 3.0 mmoles) and $IrH_3(CO)(AsPh_3)_2$ (0.5 g, 0.6 mmoles) were heated at 80° in 30 ml of benzene for 2 h. The mixture was carefully monitored and at the appearance of a band in the infrared spectrum at 2037 cm^{-1} the reaction was stopped. The solution was taken to dryness under reduced pressure, the residue was washed well with ethanol, and then it was recrystallized from CH_2Cl_2/methanol to give 0.4 g (73%) of the off-white product, m.p. 190–195° (dec.). (Found: C, 53.48; H, 3.54; N, 3.00. $C_{41}H_{33}As_2IrN_2O$ calcd.: C, 54.08; H, 3.65; N, 3.07%.) The temperature and time of reaction were crucial for the preparation of this complex. There was essentially quantitative recovery of the unchanged trihydride complex after the starting materials were warmed together in benzene at 50–60° for 1 h. When the reactants were heated for 2 h at 110–120° in toluene, a product, not as yet identified, was obtained whose infrared spectrum exhibited a strong band at 2037 cm^{-1} and a medium band at 2216 cm^{-1}, but no band ascribable to ν(Ir–H) was present. The NMR spectrum showed no high field signal.

C. Hydridocarbonyl(cinnamonitrile)bis(triphenylphosphine)iridium, $IrH(CO)(PhCH{=}CHCN)(PPh_3)_2$. Cinnamonitrile (2.5 ml, 19 mmoles), $IrH(CO)(PPh_3)_3$ (0.25 g, 0.25 mmoles) and benzene (2.5 ml) were warmed together at 50° for 1 h. The volume of the solution was then reduced until an oily residue resulted, and this residue was taken up in benzene /hexane to give a beige solid. Recrystallization from benzene/hexane gave the off-white complex, 0.18 g (75%), m.p. 140–145 (dec). (Found: C, 63.81; H, 4.77; N, 1.65; P, 6.82. $C_{46}H_{38}IrNOP_2$ calcd.: C, 63.16; H, 4.38; N, 1.60; P, 7.08%.) The compound was also obtained from reaction of the olefin with an *in situ* preparation of $IrH(CO)_2(PPh_3)_2$ and deuteriocarbonyl(cinnamonitrile)bis(triphenylphosphine)iridium was obtained from $IrD(CO)(PPh_3)_3$.

D. Hydridocarbonyl(benzylidenemalononitrile)bis(triphenylphosphine)iridium, $IrH(CO)[PhCH{=}C(CN)_2](PPh_3)_2$. A benzene solution (10 ml) of $IrH(CO)(PPh_3)_3$ (0.5 g, 0.5 mmoles) and benzylidenemalononitrile (0.77 g, 5 mmoles) was heated to 60–70° for 1 h to give a dark yellow solution. Addition of 35 ml of methanol to the cooled solution resulted in the precipitation of a pale yellow solid which was collected and washed with methanol to give 0.36 g (80%) of the complex. This was recrystallized from CH_2Cl_2/methanol as white microcrystals, m.p. 135–145° (dec). (Found: C, 62.13; H, 3.98, N, 2.94. $C_{47}H_{37}IrN_2OP_2$ calcd.: C, 62.70; H, 4.15; N, 3.11%.) In further preparations under different conditions it became apparent that different forms or isomers were being produced, the more soluble pale yellow crystals having a higher melting point (165–185°) and a different solid state infrared spectrum, but an identical CH_2Cl_2 solution spectrum, and the same analysis as for the less soluble, white, low melting (135–145°) form. The compound deuteriocarbonyl(benzylidenemalononitrile)bis(triphenylphosphine)iridium was gotten from $IrD(CO)(PPh_3)_3$.

The dicarbonyl $IrH(CO)_2(PPh_3)_2$ reacted with benzylidenemalononitrile to give a compound that is different from the complex described above in that the Ir–H bond is not present. Also, the analysis indicates that the elements of two olefin molecules are present per one iridium atom. Further studies of this compound are in progress.

E. Hydridocarbonyl(dimethyl fumarate)bis(triphenylphosphine)iridium, $IrH(CO)(CH_3OOCCH{=}CHCOOCH_3)(PPh_3)_2$. Dimethyl fumarate (0.36 g, 2.5 mmoles) and $IrH(CO)(PPh_3)_3$ (0.5 g, 0.5 mmoles) were dissolved in 5 ml of CH_2Cl_2 to give a pale yellow solution. Addition to 10 ml of ethanol caused a colorless solution to result; this was heated at 50° for $\frac{1}{2}$ h, and then allowed to cool to room temperature whereupon very pale yellow crystals of the complex separated. The crystals were washed with ethanol, yield 0.4 g (90%). (Found: C, 57.82; H, 4.54. $C_{43}H_{39}IrO_5P_2$ calcd.: C, 58.01; H, 4.42%.)

F. Dimethyl maleate (3.6 ml, 29 mmoles) and $IrH(CO)(PPh_3)_3$ (0.5 g, 0.5 mmoles) were added to 10 ml of benzene and heated at 60–70° for 10 min to give a pale yellow solution. The volume was reduced to 5 ml, ethanol (15 ml) was added, and the clear solution was placed in a refrigerator. After two weeks a white solid had separated. The solid was collected and washed with ethanol to give 0.35 (80%) of an off-white solid. The NMR and infrared spectra of this material are identical to those of the complex derived from dimethyl fumarate as described in (*E*) above, and this compound obtained from dimethyl maleate is believed (see Results and Discussion) to be hydridocarbonyl(dimethyl fumarate)bis(triphenylphosphine)iridium. (Found: C, 57.29; H, 4.73. $C_{43}H_{39}IrO_5P_2$ calcd.: C, 58.01; H, 4.42%.)

G. Hydridocarbonyl(fumaric acid)bis(triphenylphosphine)iridium, IrH(CO)-(HOOCCH=CHCOOH)(PPh$_3$)$_2$. To 1.5 ml of an ethanol solution of fumaric acid (0.06 g, 0.5 mmoles) was added dropwise a warm (70°) solution of $IrH(CO)(PPh_3)_3$ (0.25 g, 0.25 mmoles) in 2 ml of benzene. A clear, colorless solution was obtained initially, but it changed to pale yellow and a white precipitate formed as the addition was completed. The mixture was cooled to room temperature and the complex was collected, 0.11 g (50%), m.p. 192–195 (dec). (Found: C, 56.70; H, 4.11. $C_{41}H_{35}IrO_5P_2$ calcd.: C, 57.12; H, 4.10%.) An infrared spectrum of the filtrate showed bands at 2010 s, 2111 vs, and 2162 w corresponding to the protonated cation $[IrH_2(CO)(PPh_3)_3]^+$. The complex $IrH(CO)(HOOCCH{=}CHCOOH)(PPh_3)_2$, which was also prepared from $IrH(CO)_2(PPh_3)_2$, is sparingly soluble in benzene and dichloromethane, and partially soluble in methanol. When it was suspended in ethanol containing excess fumaronitrile and heated to 70°, a clear, colorless solution resulted, which upon cooling deposited crystals of the fumaronitrile complex $IrH(CO)(NCCH{=}CHCN)(PPh_3)_2$.

H. Chlorocarbonyl(fumaronitrile)bis(triphenylarsine)iridium, IrCl(CO)(NC-CH=CHCN)(AsPh$_3$)$_2$. Fumaronitrile (0.39 g, 5 mmoles) and $IrCl(CO)(AsPh_3)_2$ (0.21 g, 0.25 mmoles) were stirred together in 5 ml of CH_2Cl_2. When the yellow solution became colorless it was evaporated to dryness and the residue was washed well with EtOH to give 0.22 g (81%) of the complex, m.p. 255–260° (dec.). (Found: C, 52.00; H, 3.31; N, 2.81. $C_{41}H_{31}As_2IrN_2O$ calcd.: C, 52.01; H, 3.41; N, 2.96%.)

III. Analyses and instrumentation

Analyses for C, H, and N were carried out by Mr. R. Seab of the Department of Chemistry, Louisiana State University. Phosphorus analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Infrared spectra in the NaCl region were measured with a Beckman IR-7 spectrophotometer in Nujol or hexachlorobutadiene mulls and in dichloromethane solutions.

Molecular weights were measured using a Hewlett–Packard osmometer, Model 302A, with a 37° probe. Chloroform was the solvent.

Decomposition temperature of the compounds were obtained with a Fisher–Johns melting point apparatus.

Nuclear magnetic resonance data were gotten with Varian A-60 and HA-100 instruments using $CDCl_3$ (τ 0–10) and CH_2Cl_2 (τ 15–35) as solvents with tetramethylsilane as an internal standard.

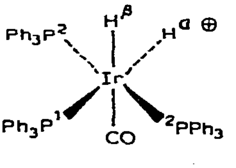
RESULTS AND DISCUSSION

Reactions of several activated olefins, *viz.*, fumaronitrile, cinnamonitrile, benzylidenemalononitrile, dimethyl fumarate, dimethyl maleate, and fumaric acid, with at least one or more of the substrates $IrH(CO)(PPh_3)_3$, $IrH(CO)_2(PPh_3)_2$, or IrH_3-

$(CO)(PPh_3)_2$ at moderate temperatures (25–75°) have resulted in displacement of triphenylphosphine, carbon monoxide, or hydrogen respectively to give complexes of the type $IrH(CO)$(activated olefin)$(PPh_3)_2$. These new compounds and their spectral properties are given in Table 1. Attempts to displace triphenylphosphine from $IrH(CO)(PPh_3)_3$ were tried with several other olefins, including 1,1-diphenylmaleonitrile, tetrachloroethylene, trichloroethylene, and cinnamaldehyde, but reactions did not occur. Maleic anhydride gave a dark mixture and a product was not isolated. Tetracyanoethylene and acrylonitrile react readily with these iridium substrates to give novel products which are not analogous to the complexes reported herein, and which have already been described[1,9].

The carboxyl-substituted olefins, maleic and cinnamic acid, reacted rapidly with $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$, and it was at first believed on the basis of infrared results that hydrido-π-olefinic complexes analogous to those mentioned above had been obtained, but further investigation has shown that this is not the case. Rather, the protonated cations $[IrH_2(CO)(PPh_3)_3]^+$ and $[IrH_2(CO)_2(PPh_3)_2]^+$ are formed. The former cation was first isolated by Malatesta *et al.*[12] as the perchlorate salt and a structure was proposed by Vaska on the basis of infrared data[14]. Collman *et al.*[15] isolated the $[IrH_2(CO)_2(PPh_3)_2]^+$ cation as the hexafluorophosphate salt and proposed the structure for this cation also on the basis of infrared data. Recently, NMR spectral data for mixtures of $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ with saturated organic acids, *e.g.*, propionic and trifluoroacetic, have been reported[16]. In the investigation reported herein, infrared and NMR spectra were obtained using CH_2Cl_2 solutions of the iridium substrates containing an excess of the unsaturated organic acid. Maleic acid in a two-fold excess was found to completely protonate both $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$; no parent substrate or hydrido-π-olefin complex was detectable in the solutions by infrared or NMR measurements. When maleic acid is added to solutions of the two iridium complexes the original yellow colors of the complex solutions are completely discharged, but with cinnamic acid, even in a five- to ten-fold excess, the yellow color was not lost. Spectral data show that some of the starting materials, as well as the protonated species, were present in these solutions. Fumaric acid, as noted in the experimental part, produces a mixture of the protonated species and the hydrido-π-olefinic complex, and the latter compound was easily isolated because of its insolubility. In summary then, the reactions of the unsaturated organic acids with $IrH(CO)(PPh_3)_3$ and $IrH(CO)_2(PPh_3)_2$ may give either protonated species or a hydrido-π-olefinic complex, with the former being favored as the strength of the organic acid increases. The tendency to protonate the iridium decreased in the order of the acid as: maleic > fumaric > cinnamic and the pK_a values for these acids are 1.9, 3.0 and 4.4 respectively.

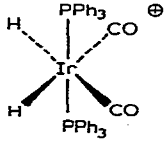
Of the four possible geometrical isomers for $[IrH_2(CO)(PPh_3)_3]^+$, only one is produced in these reactions, and the structure is believed to be (I) on the basis of the



(I)

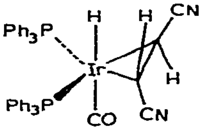
NMR spectrum, which consists of two triplets at τ 20.86 and 21.98 and a multiplet centered at τ 19.56. The higher field triplets, all members of which are split into doublets, have the same separation at 60 and 100 MHz, and are interpreted as being due to resonance of H^{α}. Thus H^{α} is split by the *trans* P^1 [$J(H^{\alpha}-P^1)$ 112 Hz], and these signals are further split by the two equivalent P^2 atoms to give triplets with $J(H^{\alpha}-P^2)$ 19 Hz. Coupling of H^{α} with H^{β} [$J(H^{\alpha}-H^{\beta})$ 4 Hz] produces additional splitting. The multiplet at τ 19.56 is due to H^{β} and arises from H^{β} coupling to the P^2 atoms [$J(H^{\beta}-P^2)$ 19 Hz] giving a triplet that is split by P^1 [$J(H^{\beta}-P^1)$ 12 Hz] into two overlapping triplets. All members of these two overlapping triplets are split into doublets due to H^{α} and H^{β} coupling, $J(H^{\alpha}-H^{\beta})$ being 4 Hz, *i.e.*, the same value as was deduced from the H^{α} pattern. Additional evidence that the reaction of maleic acid with these iridium substrates gives a compound in which the olefinic acid is not π-bonded to the metal comes from the observation that trichloroacetic acid reacts with $IrH(CO)(PPh_3)_3$ to give a solution that has infrared and NMR spectra identical to spectra of a solution of $IrH(CO)(PPh_3)_3$ and maleic acid. The spectrum of the cation $[IrH_2(CO)_2(PPh_3)_2]^+$, which is formed in the reactions of the dicarbonyl $IrH(CO)_2(PPh_3)_2$ with maleic and cinnamic acids, shows a symmetric triplet centered at τ 20.0 with $J(P-H)$ 15 Hz; an equivalency of phosphorus and hydrogen atoms is suggested (II).

An equally probable *trans* arrangement of H atoms is ruled out on the basis of the infrared spectrum, *i.e.*, two bands ascribable to $\nu(Ir-H)$ at 2170 and 2155 cm^{-1} are observed.



(II)

An X-ray study[10] of $IrH(CO)(fumaronitrile)(PPh_3)_2$ has shown that in the solid state a trigonal bipyramidal configuration exists around the iridium atom with the olefin and phosphine ligands in the equatorial plane (III).



(III)

That the H and CO ligands are *trans* to one another in the solid state is also evident from a comparison of the infrared data of Table 1. A shift[17-19] in $\nu(C{\equiv}O)$ in going from the hydrido to the deuterio complex is a criterion for a *trans* arrangement of H and CO, and it is seen from Table 1 that the complexes containing fumaronitrile, cinnamonitrile, and benzylidenemalononitrile have such a solid state arrangement. Also, in CH_2Cl_2 solution, using this same criterion, the fumaronitrile and benzylidenemalononitrile complexes have H and CO *trans* to one another.

^1H NMR data for the hydrido-π-olefinic complexes and some related compounds are listed in Table 2. Well resolved spectra were obtained for the fumaronitrile and dimethyl fumarate complexes, but the fumaric acid complex was too insoluble to obtain a spectrum and the cinnamonitrile complex, perhaps because of its tendency

TABLE 1

NEW HYDRIDO(DEUTERIO) π-OLEFINIC COMPLEXES OF IRIDIUM AND INFRARED SPECTRAL DATA[a]

Compound[b]	Medium	ν(C≡N)	ν(Ir–H)[c]	ν(C≡O)	δ(Ir–H)[f]
$IrH(CO)(FUMN)L_2$	HCBD[b]	2215 m	2105 s	1987 vs	830
	CH_2Cl_2	2211 m	2115 m	1995 vs	855
$IrD(CO)(FUMN)L_2$	HCBD	2210 m		2021 vs	
	CH_2Cl_2	2213 m		2023 vs	
$IrH(CO)(FUMN)(AsPh_3)_2$	HCBD	2211 m	2080 s	1972 vs	822, 869
	CH_2Cl_2	2214 m	2094 m	1982 vs	815, 872
$IrH(CO)(CINN)L_2$	HCBD	2210 m	2092 s	1963 vs	870, 888
	CH_2Cl_2	2208 m	2108 m	1974 vs	900
$IrD(CO)(CINN)L_2$	HCBD	2210 m		1985 vs	
$IrH(CO)(BMN)L_2$	HCBD	2213 m	2108 s	1985 vs	807, 819,
		2225 sh		1995 sh	889
	CH_2Cl_2	2220 m	2116 m	1992 vs	820–830
$IrD(CO)(BMN)L_2$	HCBD	2213 m		2019 s	
		2227 sh		2034 sh	
	CH_2Cl_2	2221 m		2021 vs	
$IrH(CO)(FUMA)L_2$[d]	HCBD		2123 s	1992 vs	816, 890
$IrH(CO)(DFUM)L_2$[e]	HCBD		2105 m	1979 vs	882, 896
$IrCl(CO)(FUMN)L_2$	Nujol	2210 m		2011 vs	

[a] In cm^{-1}. [b] Abbreviations: L = PPh_3; FUMN = fumaronitrile; CINN = cinnamonitrile; BMN = benzylidenemalononitrile; FUMA = fumaric acid; DFUM = dimethyl fumarate; HCBD = hexachlorobutadiene. [c] A common characteristic of these hydrido complexes is a decrease in intensity of the ν(Ir–H) band relative to ν(C≡N) and ν(C≡O) in going from solid state spectra to solution spectra. [d] ν(C=O) bands of organic moiety is observed at 1650 cm^{-1} as a strong absorption. [e] ν(C=O) bands of organic moiety are observed at 1685 and 1700 cm^{-1} as strong absorptions. [f] Intensities of all δ(Ir–H) bands are weak.

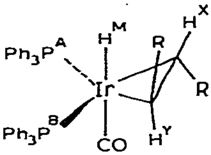
TABLE 2

^1H NMR DATA FOR NEW HYDRIDOIRIDIUM COMPLEXES[a]

Compound	Low field (τ 0–10)	High field (τ 10–35)
$IrH(CO)(FUMN)(PPh_3)_2$	7.03 m, 7.56 m[b]	21.22 m[c]
$IrCl(CO)(FUMN)(AsPh_3)_2$	7.16 d, 6.80 d($J(H_X–H_Y)$8)	
$IrH(CO)(FUMN)(AsPh_3)_2$	7.24 d, 7.08 d($J(H_X–H_Y)$ 7)[d]	21.76 t[e]
$IrH(CO)(BMN)(PPh_3)_2$	6.2 br	20–21 m
$IrH(CO)(DFUM)(PPh_3)_2$	6.4–6.6 br, 6.66(s, CH_3), 7.04(s, CH_3)	21.60 m[f]
$IrH(CO)(FUMA)(PPh_3)_2$	Too insoluble	
$IrH(CO)(CINN)(PPh_3)_2$	7.6 br	21.0–21.5[g]

[a] NMR spectra were recorded at 100 MHz in $CDCl_3$ for the low field region and CH_2Cl_2 for the high field region. Tetramethylsilane was the internal standard. Chemical shifts are given in τ units and abbreviations are: s = singlet; d = doublet; t = triplet; br = broad; m = multiplet. Phenyl proton data are not included. [b] At 60 MHz the two multiplets overlap. [c] The multiplet is a four-line pattern with each line being split into a triplet. The multiplet is interpreted as the M portion of an ABMXY pattern (see Results and Discussion). [d] The two doublets are split due to coupling with the hydrogen bound to iridium (J 1.5 Hz). Irradiation of the high field signal at τ 21.76 removes the splitting in the doublets. [e] The high field triplet collapses to a singlet when the low field signal is irradiated at τ 7.15. [f] Four-line pattern similar to high field signal of $IrH(CO)(FUMN)(PPh_3)_2$ except the two inner lines do not overlap as much. [g] The high field signal appears to be two overlapping triplets with each member showing additional splitting. Decomposition occurs in solution.

to decompose in solution, gave an unresolved spectrum. In the case of the benzylidenemalononitrile complex, a broad signal was noted at τ 6.2 and the high field signal consists of seven separate split peaks in the τ 20–21 region; perhaps these data attest to a mixture of geometrical isomers for the benzylidenemalononitrile complex. The NMR spectra generally are characterized by "olefinic" proton absorptions in the τ 6–8 range, *i.e.* values which are noticeably further upfield than the resonances in the uncoordinated olefins (τ 2–4). In the high-field region the hydrido absorption pattern is observed in the τ 20–22 region for all the complexes. These spectra are consistent with a rigidly attached, non-rotating organic moiety bonded to the iridium with the stereochemistry being the same in solution as was found for IrH(CO)(fumaronitrile)$(PPh_3)_2$ in the solid state by the X-ray structure determination. For such a rigidly bonded olefin and stereochemistry, with notation as in (IV), and ABMXY spectrum would be anticipated.



(IV)

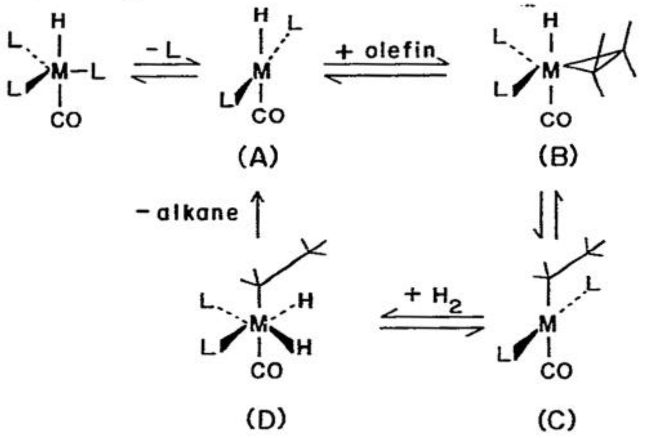
The high field spectrum of IrH(CO)(fumaronitrile)$(PPh_3)_2$ consists of a four-line pattern centered at τ 21.22 with the inner lines overlapping; each line in the four-line pattern is split into a triplet. This spectrum is interpreted as being the M portion of the ABMXY system, and the four lines arise from coupling of the two nonequivalent phosphorus atoms to the H^M proton and each line is further split by coupling to the olefinic protons H^X and H^Y. The high field spectrum was simplified by irradiating downfield at τ 7.45 to remove the H^X and H^Y coupling; in the resulting ABM pattern, as is the case in such systems[20], there is no spacing that corresponds to either $J(H^M–P^A)$ or $J(H^M–P^B)$. Rather, the outermost lines are separated by the sum $J(H^M–P^A)+J(H^M–P^B)$, which is 34 Hz for IrH(CO)(fumaronitrile)$(PPh_3)_2$ and 37 Hz for IrH(CO)(dimethyl fumarate)$(PPh_3)_2$.

Rigid attachment of an olefin such as fumaronitrile or dimethylfumarate in a structure like (IV) implies that the "olefinic" protons are not equivalent, and that this is so in these complexes is confirmed by the low-field NMR spectra. The low-field spectrum of IrH(CO)(fumaronitrile)$(PPh_3)_2$ at 100 MHz consists of two triplets centered at τ 7.03 and 7.56. The spectrum is complex with each member of each triplet being split into what appears to be a triplet. At 60 MHz the separation of the two primary triplets has decreased such that they overlap, thus showing that the two triplets are due to non-equivalent protons. We particularly wanted to know the $H^X–H^Y$ coupling constants in these kinds of compounds, and therefore prepared some related triphenylarsine complexes to obtain less complex spectra. A similar pattern which shows the non-equivalency of the olefinic protons and allows determination of $J(H^X–H^Y)$ was observed in the spectrum of IrCl(CO)(fumaronitrile)$(AsPh_3)_2$. The pattern consists of two doublets centered at τ 7.16 and τ 6.80 with $J(H^X–H^Y)$ 8 Hz. In the spectrum of the hydrido analog, IrH(CO)(fumaronitrile)$(AsPh_3)_2$, the XY part, *i.e.* at low field, of the MXY spectrum consists of two doublets centered at τ 7.08 and τ 7.24 with small splitting ($J \approx 2$ Hz) due to the hydrogen attached to iridium. The high field pattern appears as a triplet centered at τ 21.76, and this signal collapsed to a singlet when the downfield signal was irradiated at τ 7.15. On the other hand, when the high-field signal was irradiated at τ 21.76, the expected pattern of two doublets was observed downfield with $J(H^X-H^Y)$ 7 Hz. Thus, these data not only yield information about the structures of the complexes but they also say something about the nature of bonding in these compounds. The point to be made here is that the magnitude of the coupling constants, *i.e.* $J(H^X-H^Y)$, suggests that an "iridacyclopropane" appellation may be appropriate for these complexes. Whereas a range of values from 13 to 18 Hz has been reported[21] for the coupling between *trans*-hydrogen atoms in –CH=CH– systems, lower values are seen for *trans*-hydrogen atoms in three-membered ring compounds, *viz.* 6.99 Hz for bromocyclopropane[22] and 5.58 Hz for cyclopropane[23].

Several years ago Vaska reported[24] that $IrH(CO)(PPh_3)_3$ was a catalyst for the homogeneous hydrogenation of ethylene at ambient conditions and more recently the isostructural complex $RhH(CO)(PPh_3)_3$ has been shown to be an effective, highly selective catalyst for the homogeneous hydrogenation of terminal olefins in a detailed kinetic study by O'Connor and Wilkinson[25]. In these catalytic studies employing non-activated olefins, mechanistic schemes were proposed which included hydrido-π-olefinic complexes as intermediates, but such complexes were not isolated. It is, therefore, of interest that now these model compounds have been prepared, and their relevance to homogeneous catalysis will be discussed in the context of one of the proposed mechanisms, which is shown in Scheme 1.

SCHEME 1

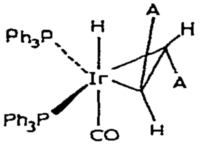
PROPOSED MECHANISM FOR HOMOGENEOUS HYDROGENATION OF OLEFINS CATALYZED BY $MH(CO)(L)_3$ ($M=Rh$, Ir; $L=PPh_3$)



First of all, the isolation of the complexes $IrH(CO)$(activated olefin)$(PPh_3)_2$, which are analogous to intermediate (B) of Scheme 1, gives credence to the proposed mechanism. As depicted in the mechanistic scheme, the isolated compounds have a structure in which the hydride is *cis* to the π-bonded olefin, and a hydride transfer [(B) → (C)] via a four-center transition state is easily visualized. Attempts to duplicate this step by thermal means with either $IrH(CO)$(cinnamonitrile)$(PPh_3)_2$ or the fumaronitrile complex were not successful. Thus, heating $IrH(CO)$(fumaronitrile)$(PPh_3)_2$

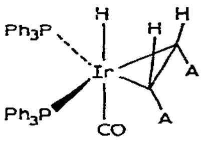
in toluene at 110° for 1 h led only to recovery of the compound, and heating it in xylene at 140° for 4 h gave a dark mixture from which no complex could be recovered. Attempts to duplicate the entire cycle of Scheme 1 by conversion of fumaronitrile into succinonitrile under catalytic conditions using $IrH(CO)(PPh_3)_3$ as a potential catalyst did not succeed. Hydrogen gas was bubbled through a benzene solution of $IrH(CO)(PPh_3)_3$ (10^{-3} *M*) and fumaronitrile (10^{-1} *M*) at room temperature for 1h at which time an infrared spectrum of the solution showed the presence of fumaronitrile and $IrH(CO)(fumaronitrile)(PPh_3)_2$ but no succinonitrile. Under similar conditions the rhodium complex $RhH(CO)(PPh_3)_3$, which is known to be a better hydrogenation catalyst than the iridium analog, also did not catalyze the hydrogenation of fumaronitrile. However, succinonitrile was obtained when the catalyst $RhCl(PPh_3)_3$ was employed under the same conditions.

While $IrH(CO)(PPh_3)_3$ has not been found to be a catalyst for hydrogenation of fumaronitrile at ambient conditions, it does function as a catalyst for isomerization of dimethyl maleate to dimethyl fumarate. We noted in the Experimental that the product obtained from the reaction of the *trans* olefin dimethyl fumarate with $IrH(CO)(PPh_3)_3$ had the same infrared and NMR spectra as the product obtained from the analogous reaction using the *cis* olefin dimethyl maleate. Further, the non-equivalency of the OCH_3 protons in the NMR spectrum is consistent with (V) rather than (VI) or (VII), and the high field ABMXY pattern rules out the possibility of a mixture of (VI) and (VII) (which could possibly give different OCH_3 signals) because an A_2MX_2 pattern would be expected.

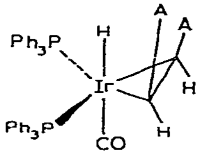


(V)

A= COOMe



(VI)



(VII)

It thus appears that isomerization of the *cis* olefin to the *trans* form occurs somewhere during the course of the reaction of dimethyl maleate with $IrH(CO)(PPh_3)_3$. That $IrH(CO)(PPh_3)_3$ will function catalytically in this process was shown as follows. Two samples (2 ml) of dimethyl maleate, one of which contained 0.6 mole% of $IrH(CO)(PPh_3)_3$, were heated at 100° in an oil bath, and portions were withdrawn periodically for examination via NMR to determine the relative amounts of *cis* and *trans* olefin present. After two hours no isomerization had occurred in the control sample, but the sample containing the complex consisted of approximately equal amounts of dimethyl maleate and dimethyl fumarate.

The very fact that the complexes $IrH(CO)(activated\ olefin)(PPh_3)_2$ are isolable may be a clue as to why $IrH(CO)(PPh_3)_3$ is not a homogeneous catalyst for hydrogenation of an activated olefin like fumaronitrile at ambient conditions as it is for the unactivated olefin ethylene. One implication is that the presence of an olefin containing electron-withdrawing substituents in the coordination sphere inhibits hydride transfer to the coordinated organic moiety. It is suggested that this behavior is related to (*a*) the orientation of the olefin with respect to the Ir–H bond axis and (*b*) the strength of the Ir–H bond. Both of these factors are believed to be affected by activated olefins such that hydride transfer is less likely. In regard to (*a*), a transition state with the Ir–H and C=C axes parallel would seem to be the most favorable orientation for H transfer, and hence a 90° rotation of the olefin is necessary for complexes such as these discussed herein. For metal–olefin complexes with electron-withdrawing substituents attached to the olefin carbon atoms, in the context of the Dewar–Chatt–Duncanson model of bonding, the metal→olefin π-bond would be expected to be stronger and the olefin→metal σ-bond would be expected to be weaker relative to analogous components in a conventional metal–olefin complex. Hence the net result would be that rigidity of the $\mathrm{M}\begin{smallmatrix}\diagup\mathrm{C}\\ \diagdown\mathrm{C}\end{smallmatrix}$ framework in activated olefin complexes would be enhanced such as to be less conducive to olefin rotation relative to complexes containing olefins like ethylene where the weaker metal→olefin π-bond and the stronger olefin→metal σ-bond would lead to more facile olefin rotation. The effect, then, of electron-withdrawing substituents is believed to be such as to "lock" the olefin in a less favorable position for hydride transfer. In regard to factor (*b*), it is expected that the Ir–H bond would be stronger in those systems containing activated olefins because of the more extensive polarization of electron density from around the metal toward the olefin.

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