η^3-Allyl Metal Hydride Complexes. Oxidative Addition of Cyclopropane and Olefin Substrates to Iridium(I) Complexes. Structure of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}C_6H_5)][P(C_6H_5)_3]_2$

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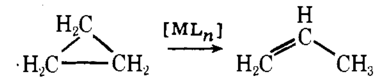
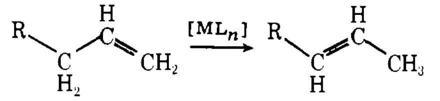
Abstract: Phenylcyclopropane reacts with *trans*-$IrCl(N_2)(PPh_3)_2$ or "$IrCl(PPh_3)_2$" to yield $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$. This complex is also obtained from similar reactions with allylbenzene or *trans*-β-methylstyrene. A series of analogous complexes is formed from the reaction of allylbenzene, $[IrCl(COT)_2]_2$ (COT = cyclooctene), and the appropriate donor ligand in which PPh_3 (Ph = C_6H_5) is replaced by $P(p\text{-Tol})_3$ (p-Tol = 4-tolyl), $AsPh_3$, $As(p\text{-Tol})_3$, or $SbPh_3$. These η^3-allyl hydride complexes do not exhibit dynamic behavior in solution as judged by their variable-temperature NMR spectra. They possess unusual thermal stability and are not highly air sensitive. Chloroform solutions of the η^3-allyl hydride complexes do not effect the conversions of cyclopropane to olefin or primary to internal olefin. The complex $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$ reacts with CO or PF_3 to liberate β-methylstyrene, which also results from the extended exposure of the complex to O_2. Reaction with HCl yields a mixture of products from which a new isomer of $IrCl_2H(CO)(PPh_3)_2$ is obtained upon treatment with CO. Similar reaction with HBr causes total substitution of chlorine. Spectroscopic data indicate that $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$ adopts a geometry in which the phosphine ligands are mutually cis, hydrido and chloro ligands are trans, and the allyl group occupies two coordination sites. This structure is substantiated by a single-crystal X-ray diffraction study. The complex crystallizes in space group $C_{2v}{}^9\text{-}Pn2_1a$ with four formula units in a cell of dimensions a = 14.902 (2), b = 11.016 (2), and c = 22.456 (4) Å. Based on 3738 unique reflections having $F_0{}^2 > 3\,\sigma(F_0{}^2)$, the structure was refined by full-matrix least-squares techniques to conventional agreement indices (on F) of R = 0.029 and R_w = 0.041. The hydride and allyl hydrogen atoms were located and refined. The Ir-Cl bond length is long, 2.549 (2) Å, as a result of the trans influence of the hydrido ligand. The geometry of the allyl group, including hydrogen atoms, is similar to that found in other η^3-allyl complexes. The implications of the isolation of these η^3-allyl hydride complexes to catalytic transformations of cyclopropanes and olefins are discussed.

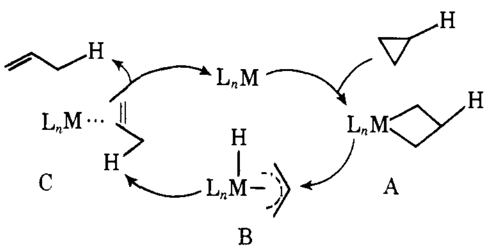
The ability of transition-metal complexes to effect structural transformations in organic substrates constitutes a basic facet of organometallic chemistry. Two such transformations which have received much attention are the metal-assisted rearrangements of strained-ring molecules, particularly the conversions of cyclopropanes to olefins (eq 1),[1] and the metal-promoted isomerizations of olefins (eq 2).[2] Allyl metal hydride (A-M-H) complexes have been implicated as key intermediates in both of these transformations. The former reaction is proposed to proceed via the mechanism presented in Scheme I. The intermediacy of an A-M-H complex, B, accounts for the variety, distribution, and stereochemistry of the observed products.[1,3-8] The initial step in the sequence, insertion of a metal center into a three-membered ring to form a metallocyclobutane complex, A, has ample precedent[9-16] and the conversion of A to C has recently also been reported.[17] However, the crucial central step, β-hydrogen abstraction[18] with concomitant formation of the A-M-H complex, B, has not been demonstrated.


(1)

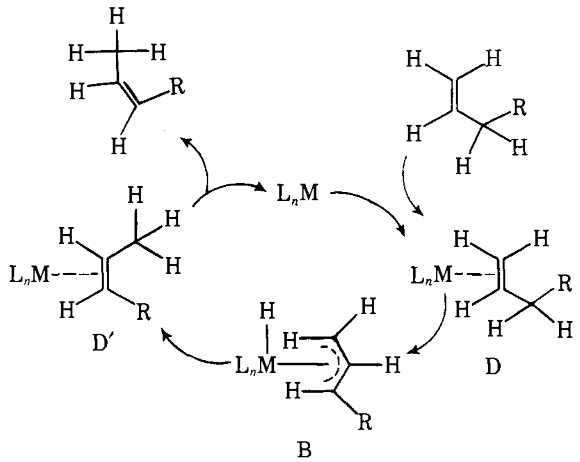


$$\mathrm{RCH_2CH{=}CH_2} \xrightarrow{[ML_n]} \mathrm{RCH{=}CHCH_3} \qquad (2)$$

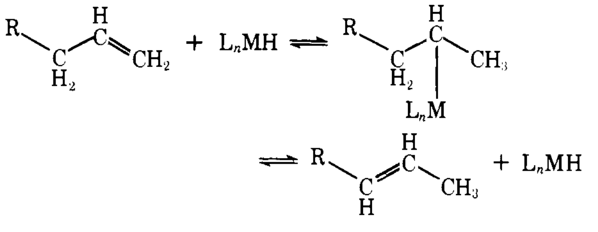
Scheme I



Scheme II



Two major mechanisms have been envisioned for the metal-promoted isomerizations of olefins. Although much less well documented than the metal hydride addition-elimination mechanism (eq 3),[2a,19-22] an allyl metal hydride mechanism[23-25] (Scheme II) has received support from detailed stereochemical studies.[26-29] However, the intermediacy of complex B has only been confirmed by direct observation in one system,[30] although dynamic equilibria between species of forms D and B have been observed in two cases.[31,32]



$$\mathrm{RCH_2CH{=}CH_2} + \mathrm{L_nMH} \rightleftharpoons \mathrm{RCH_2CH(ML_n)CH_3} \rightleftharpoons \mathrm{RCH{=}CHCH_3} + \mathrm{L_nMH} \qquad (3)$$

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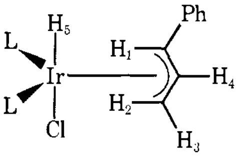
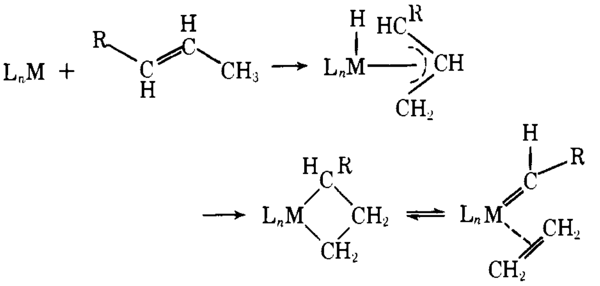
Table I. Spectral Data for $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)]L_2$



L	PPh_3	$AsPh_3$	$SbPh_3$	$P(p\text{-}Tol)_3$	$As(p\text{-}Tol)_3$
IR[a]					
ν_{Ir-H_5}, cm^{-1}	2208	2179	2152	2200	2213
^1H NMR[b]					
δ_{H_1},[c] ppm	3.90 (dd) ($J_{H_1P_{trans}} = 8.4$ Hz)	3.87 (d)	3.82 (d)	4.02 (dd) ($J_{H_1P_{trans}} = 9.1$ Hz)	3.75 (d)
δ_{H_2}	2.74 (dd) ($J_{H_2P_{trans}} = 11.3$ Hz)	2.79 (d)	2.61 (d)	2.73 (dd) ($J_{H_2P_{trans}} = 10.3$ Hz)	2.72 (d)
δ_{H_3}	2.87 (dd) ($J_{H_3P_{trans}} = 3.5$ Hz)	2.98 (d)	3.65 (d)	2.88 (dd) ($J_{H_3P_{trans}} = 4.4$ Hz)	2.95 (d)
δ_{H_4}	5.72 (ddd)	5.70 (ddd)	5.59 (ddd)	5.70 (ddd)	5.64 (ddd)
δ_{H_5}	−24.4 (dd) ($J_{H_5P} = 13.8, 16.2$ Hz)	−26.0 (s)	−27.0 (s)	−24.5 (dd) ($J_{H_5P} = 13.2, 17.0$ Hz)	−26.1 (s)
other	6.8-7.4 (m), Ph	6.7-7.3 (m), Ph	6.7-7.4 (m), Ph	6.8-7.4 (m), Ph 2.30 (s), Me	6.7-7.2 (m), Ph 2.29 (s), Me
J_{14}, Hz	10.3	10.3	10.3	10.0	10.1
J_{24}, Hz	10.7	10.9	11.0	10.9	10.8
J_{34}, Hz	7.2	7.0	6.8	7.3	6.8
^{31}P NMR[b]					
δ (ppm)[d]	1.16, 0.87			0.32, −1.30	
J_{PP}, Hz	5.0			3.8	

[a] Measured as Nujol mulls. [b] Measured as $CDCl_3$ solution at 30 °C. [c] Downfield from external Me_4Si. [d] Downfield from external 85% H_3PO_4.

The A-M-H complexes have also been suggested as precursors to the metallocyclobutane ⇌ carbene-olefin complex manifold implicated in olefin metathesis (eq 4).[33] Despite the interest in A-M-H complexes generated by these important catalyses, few such complexes have been reported. The compounds $NiH(\eta^3\text{-}C_3H_5)L$,[31] L = PPh_3 (Ph = C_6H_5) or PF_3, prepared at low temperature, decompose irreversibly above −30 °C. Between −40 and −50 °C the PF_3 complex was shown to be in dynamic equilibrium with the corresponding nickel(0)-η^2-propene complex. The complex $RhClH(\eta^3\text{-}C_3H_5)(PF_3)_2$[34] was observed at −75 °C as an intermediate in the reaction of $Rh(\eta^3\text{-}C_3H_5)(PF_3)_3$ with HCl which yields $[RhCl(PF_3)_2]_2$ and propene. Byrne et al.[32] have reported the ^1H NMR characterization of $MoH(\eta^3\text{-}C_3H_5)(dppe)_2$, dppe = $Ph_2P(CH_2)_2PPh_2$, and have shown that, although stable to 110 °C, this complex exhibits dynamic behavior similar to that observed in the nickel system. Recently the complex $RuH(\eta^3\text{-}C_3H_5)(NCCH_3)(PPh_3)_2$ has also been reported.[35]



(4)

In an earlier communication[36] we described our preliminary results concerning an iridium(III) allyl hydride complex, $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$, which is obtained from both cyclopropane and olefin starting materials. This complex exhibits exceptional stability and provides substantiation for the mechanisms shown in Schemes I and II. The isolation of this complex is also of interest as it provides an example of oxidative addition, and thus activation, of C-H and C-C bonds by metal complexes.[37] We present here the results of a more intensive study of a series of Ir(III) η^3-allyl hydride complexes, including the determination of the structure of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$.

Experimental Section

IR spectra in the range 4000-400 cm^{-1} were recorded from Nujol mulls using Perkin-Elmer 283 or Nicolet 7199 FT spectrometers. In the range 400-230 cm^{-1} samples were run as Nujol mulls between high-density polythene windows using the former spectrometer. ^1H NMR spectra were recorded on Varian CFT-20 or Hitachi Perkin-Elmer R20-B spectrometers, at 80 or 60 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were measured on a Varian CFT-20 instrument operating at 32.199 MHz. Melting points were measured for encapsulated samples with a Mel-Temp hot-stage apparatus and are uncorrected. Microanalyses were carried out by Micro-Tech Laboratories, Inc., Skokie, Ill., or Ms. Hilda Beck, Northwestern University.

All reactions and manipulations involving air-sensitive materials were carried out under inert atmosphere, either dinitrogen or argon. Phenylcyclopropane, allylbenzene, and *trans*-β-methylstyrene were obtained from Aldrich Chemical Co. and used without additional purification. These organic substrates were deoxygenated by vigorously passing a stream of dry dinitrogen through them for at least 1 h immediately prior to use. The complex *trans*-$IrCl(N_2)(PPh_3)_2$[38] was prepared by the literature procedure as was $[IrCl(COT)_2]_2$[39] (COT = cyclooctene) except that this latter complex was washed with chilled, degassed 2-propanol rather than with methanol. The use of the primary alcohol often resulted in formation of *trans*-$IrCl(CO)(PPh_3)_2$ as a minor side product in subsequent reactions. This presumably arises from decarbonylation of the traces of residual alcohol by a highly reactive Ir(I) phosphine complex.[38,40] Phosphine, arsine, and stibine ligands were obtained from commercial sources and were used as received. Solvents were dried and distilled under dinitrogen prior to use. The spectral data of the new complexes are summarized in Table I.

Preparation of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$ (1). A. A sample of *trans*-$IrCl(N_2)(PPh_3)_2$ (1.00 g, 1.3 mmol) was suspended in 8.0 mL of neat, degassed phenylcyclopropane (64 mmol). With stirring at room temperature the yellow solid slowly dissolved to form an orange solution from which an off-white solid was deposited. After 15 days the solid was collected, washed with ether and acetone, and dried in vacuo. Recrystallization from chloroform/methanol produced colorless crystals (0.47 g, 42%), mp 191 °C dec. Anal. ($C_{45}H_{40}ClIrP_2$) C, H, Cl.

B. A flask containing *trans*-$IrCl(N_2)(PPh_3)_2$ (0.50 g, 0.64 mmol) was charged with 8.5 mL (64 mmol) of freshly degassed allylbenzene and the mixture was stirred at room temperature. The yellow solid rapidly dissolved to produce a deep red solution. After 8 h the solution had become pale orange and an off-white precipitate had formed. Ether (20 mL) was added and workup proceeded as in A to yield 0.42 g (78%) of **1**.

C. The olefin *trans*-β-methylstyrene was substituted for allylbenzene in B and the reaction mixture was stirred for 12 h before addition of ether. Recrystallization gave **1** in 71% yield.

D. The compounds $[IrCl(COT)_2]_2$ (0.16 g, 0.18 mmol) and PPh_3 (0.19 g, 0.72 mmol) were vigorously stirred together as solids. Phenylcyclopropane (4.6 mL, 37 mmol) was added and a deep red solution quickly ensued. The mixture was stirred at room temperature for 18 h, at which time it had become a yellow-brown suspension. The usual workup gave **1** in 49% yield (0.15 g).

E. In a similar manner $[Ir(Cl(COT)_2]_2$ (0.19 g, 0.21 mmol), PPh_3 (0.23 g, 0.86 mmol), and allylbenzene (5.7 mL, 43 mmol) were combined to form a deep red solution. The mixture rapidly became a yellow-brown slurry. After 3 h the reaction mixture was worked up in the usual manner to yield 0.32 g of **1** (85%).

F. The compound *trans*-β-methylstyrene was substituted for allylbenzene in E and the reaction mixture stirred for 12 h. Workup gave **1** in 79% yield.

Preparation of Other η^3-Allyl Hydrides, $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)]L_2$. L = $AsPh_3$ (2). Samples of $[IrCl(COT)_2]_2$ (0.20 g, 0.22 mmol), $AsPh_3$ (0.27 g, 0.88 mmol), and allylbenzene (5.8 mL, 44 mmol) were combined as in E. A white solid rapidly formed and the mixture was worked up after 2 h to yield **2** (0.29 g, 69%), mp 221 °C dec. Anal. ($C_{45}H_{40}As_2ClIr$) C, H, Cl.

Complexes 3, 4, and 5 (L = $SbPh_3$, $P(p\text{-}Tol)_3$, and $As(p\text{-}Tol)_3$ (*p*-Tol = 4-Tolyl), Respectively). These complexes were prepared in a similar manner using the appropriate donor ligand, a reaction time of 18 h, and a 50-fold, rather than 100-fold, excess of allylbenzene. Complex **3** was recrystallized from chloroform/methanol (30% yield), while **4** and **5** were recrystallized from dichloromethane/methanol in 63 and 52% yields, respectively. Complex **3**: mp 198 °C dec. Anal. ($C_{45}H_{40}ClIrSb_2$) C, H, Cl. Complex **4**: mp 146 °C dec. Anal. ($C_{51}H_{52}ClIrP_2$) C, H. Complex **5**: mp 166 °C dec. Anal. ($C_{51}H_{52}As_2ClIr$) C, H.

Similar procedures using other donor ligands (PEt_3, PMe_2Ph, $PMePh_2$, $P(o\text{-}Tol)_3$ (*o*-Tol = 2-tolyl), dppe, $P(OPh)_3$) failed to yield the desired η^3-allyl metal hydride complexes. In all reactions the residual substrate mixture was isolated from the supernatant mixture by vacuum distillation at room temperature and its ^1H NMR spectrum recorded in order to ascertain the extent of any isomerization. In the absence of metal complexes no isomerization was detected for any of the substrates.

Reaction of 1 with CO. Into a dichloromethane (5 mL) solution of **1** (36 mg, 0.041 mmol) at room temperature and pressure CO was bubbled for 15 min during which time the solution became yellow. The solution was allowed to stand under a CO atmosphere for an additional 15 min. Upon addition of methanol (20 mL) a yellow solid precipitated. Recrystallization from chloroform/methanol (1:1) gave yellow crystals of *trans*-$IrCl(CO)(PPh_3)_2$ (28 mg, 84%). The identity of this complex was verified by comparison with an authentic sample [ν_{CO} 1960 cm^{-1}, $\nu_{Ir\text{-}Cl}$ 313, 311 (sh) cm^{-1}]. Anal. ($C_{37}H_{30}ClIrOP_2$) C, H, Cl.

In an alternative experiment, CO was bubbled into a deuteriochloroform solution of **1** in an NMR tube. In the ^1H NMR spectrum of the resulting solution the resonances of the allyl and hydrido ligands were completely replaced by those of β-methylstyrene, as verified by comparison with an authentic sample.

Reaction of 1 with PF_3. PF_3 was substituted for CO in the above procedures and *trans*-$IrCl(PF_3)(PPh_3)_2$ was isolated in 75% yield as a yellow solid. Its identity was verified by comparison with an authentic sample[40,41] [$\nu_{Ir\text{-}Cl}$ 300 cm^{-1}]. Anal. ($C_{36}H_{30}ClF_3IrP_3$) C, H. β-Methylstyrene was the only hydrocarbon product observed by NMR spectroscopy.

Reaction of 1 with O_2. A saturated solution of **1** in $CDCl_3$ in an NMR tube was flushed with dry O_2 for 10 min. The system was then sealed and stored at room temperature. The solution gradually became green and ^1H NMR spectroscopy indicated the slow production of β-methylstyrene. After 10 weeks the solution was concentrated to yield a mixture of **1** and the green product, which could be separated by extraction with acetone. The IR spectrum of the green solid shows bands at 1120 and 720 cm^{-1} characteristic of $OPPh_3$ and is identical with that of authentic samples of the oligomeric dioxygen-decomposition products of *trans*-$IrCl(N_2)(PPh_3)_2$[38] and "$IrCl(PPh_3)_2$".[42]

Reaction of 1 with HCl. Anhydrous HCl was bubbled into a saturated $CDCl_3$ solution of **1** in an NMR tube. The solution immediately turned yellow and in its ^1H NMR spectrum there were no resonances arising from **1**. These were replaced by those of both β-methylstyrene and allylbenzene, in approximately equal intensity. The upfield hydride signal of **1** had been replaced by two sets of triplets of approximately equal intensity at δ −23.2 and −24.0 ($^2J_{PH}$ = 19.5, 19.8 Hz, respectively).

In a separate experiment, 0.23 g (0.26 mmol) of **1** was dissolved in 20 mL of dichloromethane. Anhydrous HCl was bubbled into the solution for 10 min and the solution was concentrated. Recrystallization from benzene-*n*-hexane yielded 0.19 g of pale yellow solid (92% based on $IrCl_2H(PPh_3)_2$). Anal. ($C_{36}H_{31}Cl_2IrP_2$) C, H, Cl: calcd, 8.0; found, 8.7. The ^1H NMR spectrum of this solid shows hydride resonances equivalent to those observed above. The IR spectrum contains a weak, broad band centered at ca. 2260 cm^{-1} which we ascribe to $\nu_{Ir\text{-}H}$.

Reaction of $IrCl_2H(PPh_3)_2$ with CO. Into a CH_2Cl_2 solution of $IrCl_2H(PPh_3)_2$, prepared in situ from **1**, was bubbled CO. The yellow solution rapidly decolorized and an off-white solid began to precipitate almost immediately. After 5 min the addition of CO was discontinued and the volume of the suspension reduced. Ether was added and the resulting suspension was filtered to yield an off-white solid in quantitative yield. Anal. ($C_{37}H_{31}Cl_2IrOP_2$) C, H, Cl. The IR spectrum shows bands at 2245 ($\nu_{Ir\text{-}H}$), 2078 (ν_{CO}), 300, and 260 ($\nu_{Ir\text{-}Cl}$) cm^{-1}.

Reaction of 1 with HBr and CO. A saturated CH_2Cl_2 solution of **1** was treated sequentially with anhydrous HBr and CO in the manner employed above for HCl and CO. The off-white solid obtained contains no chlorine. Anal. ($C_{37}H_{31}Br_2IrOP_2$) C, H. Bands at 2240 ($\nu_{Ir\text{-}H}$) and 2070 (ν_{CO}) cm^{-1} are present in the IR spectrum.

Collection and Reduction of the X-ray Data. Vapor diffusion of acetone into a dichloromethane solution of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$ (**1**) yielded a crop of colorless, rectangular needles suitable for diffraction. Preliminary photographic data from a crystal mounted in air indicated that the crystal belongs to the orthorhombic system. Systematic extinctions ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) characteristic of the space groups $D_{2h}{}^{16}$-*Pnma* and $C_{2v}{}^{9}$-$Pn2_1a$ were observed. Crystallographic data are tabulated in Table II. The observed density is in accord with four molecules per unit cell. Consequently in the centrosymmetric group $D_{2h}{}^{16}$-*Pnma*, in the absence of disorder, the molecule must contain either a center or a plane of symmetry. As spectroscopic data do not indicate either type of molecular symmetry, the polar noncentrosymmetric group $C_{2v}{}^{9}$-$Pn2_1a$ was chosen initially. This choice was subsequently shown to be correct as reasonable positional and thermal parameters, including those of the allylic and hydride hydrogen atoms, were refined successfully.

Cell constants (Table II) were obtained as previously described[43] by a least-squares refinement of 15 reflections manually centered on a Picker FACS-I diffractometer. These reflections were generated using a narrow source and chosen from diverse regions of reciprocal space [$55.1° \leq 2\theta(\text{Cu } K\alpha) \leq 59.9°$].

Intensity data were collected on the diffractometer in shells of 2θ using the θ–2θ scan technique. Background counts were measured at both ends of the scan range with both the counter and crystal held stationary. If the observed peak intensity was less than 3σ, as defined by the background counting statistics, the reflection was rescanned and each background recounted for twice its original time. The results of the two scans and two backgrounds were then combined. For 2θ less than 40° the intensities of $+h$, $\pm k$, $+l$ reflections were collected to provide data from Friedel pairs for the determination of the correct enantiomer (vide infra). Only $+h$, $+k$, $+l$ data were collected for 2θ greater than 40°. Six of every 100 reflections were measured as standards for $2\theta \leq 124.5°$. For higher values of 2θ, three standard

Table II. Summary of Crystal Data and Intensity Collection

compd	$IrClH[\eta^3-C_3H_4(1-Ph)](PPh_3)_2$
formula	$C_{45}H_{40}ClIrP_2$
formula weight	870.42 amu
a	14.902 (2) Å
b	11.016 (2) Å
c	22.456 (4) Å
V	3686 Å^3
Z	4
ρ_{calcd}	1.568 g/cm^3
ρ_{obsd}	1.57 (1) g/cm^3
space group	$C_{2v}{}^9$-$Pn2_1a$
crystal dimensions	0.70 × 0.36 × 0.34 mm
crystal shape	rectangular rod with major faces of the forms {101}, {111}, and {0$\bar{1}$0}
crystal volume	0.0182 mm^3
temp	22 °C
radiation	Cu Kα [λ(Cu Kα_1) 1.540 562 Å] prefiltered through 1-mil Ni foil
μ	86.3 cm^{-1}
transmission factors	0.159-0.379
receiving aperture	2.2 × 2.8 mm; 30 cm from crystal
takeoff angle	3.5°
scan speed	2° in 2θ/min
scan range	0.8° below Kα_1 to 0.8° above Kα_2 for $2\theta \leq 124.5°$, 0.9 below Kα_1 to 0.9 above Kα_2 for $2\theta > 124.5°$
background counts	10 s at each end of scan with rescan option (see text)
2θ limits	5.0-160.0°
observations	$2\theta \leq 40°$ $+h, \pm k, +l$ $2\theta > 40°$ $+h, +k, +l$
total no. of observations	4346
unique data, $F_o{}^2 > 3\sigma(F_o{}^2)$; $+h, +k, +l$	3738
final no. of variables	168
R	0.029
R_w	0.041
error in observation of unit weight	1.58 electrons

reflections were measured. No significant deviations in the intensities of these standards were observed. The data were processed as described previously,[44] using a p value of 0.04. An absorption correction was applied to the data.[45] The total number of independent data with $F_o{}^2 > 3\sigma(F_o{}^2)$ was 3738. Only $+k$ data were used in the solution and preliminary refinement of the structure.

Solution and Refinement of the Structure. The iridium atom was located from an origin-removed Patterson synthesis. Structure factor and Fourier synthesis calculations revealed the positions of the phosphorus and chlorine atoms. Subsequently, the positions of the remaining nonhydrogen atoms were obtained by the usual combination of least-squares refinements and difference Fourier syntheses. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are respectively the observed and calculated structure amplitudes and where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$. Atomic scattering factors for the nonhydrogen atoms were taken from the usual tabulation.[46] Anomalous dispersion terms were not included at this stage of refinement. The phenyl rings were treated as rigid groups[27] and restricted to a geometry having uniform C-C distances of 1.395 Å and ideal D_{6h} symmetry. Each of the group atoms was refined with an individual isotropic thermal parameter. Refinement of the structure with all nonhydrogen atoms included as isotropic bodies resulted in agreement indices of $R = 0.073$ and $R_w = 0.104$, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$.

A test was next made to determine the correct enantiomer for this crystal. Separate least-squares calculations for the two enantiomers were carried out in which all of the nongroup atoms were allowed to vibrate anisotropically and the anomalous dispersion terms for Ir, Cl, and P atoms were included.[48] In these calculations $-k$ data were included. In the first calculation the original enantiomer refined to $R = 0.054$ and $R_w = 0.087$. The same least-squares calculation for the alternative enantiomer yielded agreement indices of $R = 0.057$ and $R_w = 0.090$. In view of the absence of a dramatic difference in these agreement indices we performed a subsequent comparison of Friedel pairs.

Of the 138 Friedel pairs collected, 35 (for which $F_c \geq 20e$ and $||F_c(khl)| - |F_c(h\bar{k}l)||/|F_c(hkl)| > 0.05$) were compared. Of this number the trend among 34 confirmed the original enatiomer as the correct choice.

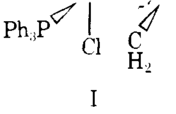
The positions of the hydrogen atoms of the allyl and phenyl groups were determined from ideal geometries and a C-H distance of 0.95 Å. Each of these 39 hydrogen atoms was then assigned an isotropic thermal parameter 1 Å^2 greater than that of the carbon atom to which it is attached. These atoms were included in subsequent calculations as fixed contributions. The hydrogen atom scattering factors used were those of Stewart et al.[49] After a cycle of least-squares refinement a difference Fourier synthesis revealed the position of the hydride hydrogen atom. This atom was refined as an isotropic body in subsequent calculations. The fixed contribution of the phenyl hydrogen atoms was reset, based on the new positions of the group carbon atoms. Rather than being included with the fixed contributions, the hydrogen atoms of the allyl group were allowed to vary isotropically in the final cycles of refinement. These calculations converged to final agreement indices of $R = 0.029$ and $R_w = 0.042$. The error in an observation of unit weight is 1.58 electrons. The largest peaks in the final difference Fourier synthesis are approximately 0.57e$^-$ Å^{-3} and are associated with the iridium atom. An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices reveals no unexpected trends.

The final positional and thermal parameters of the nonhydrogen atoms appear in Table III. Table IV lists the derived parameters of the 42 group atoms. The root-mean-square amplitudes of vibration and the idealized positions for the phenyl hydrogen atoms are given in Tables V and VI, respectively.[50] A listing of the observed and calculated structure amplitudes is also available.[50]

Results

Syntheses and Reactions. When a suspension of *trans*-$IrCl(N_2)(PPh_3)_2$ in neat phenylcyclopropane is stirred at room temperature the yellow solid dissolves slowly to yield an orange solution from which an off-white solid, $IrClH[\eta^3-C_3H_4(1-Ph)](PPh_3)_2$ (**1**), is deposited. No Ir(III) complex is obtained when benzene or toluene is used as solvent. Complex **1** is sparingly soluble in THF and chlorinated hydrocarbons but insoluble in benzene, toluene, ether, or hydrocarbon solvents. It is stable indefinitely in air in the solid state and decomposes only very slowly in solution on exposure to the atmosphere (vide infra). The most prominent feature of the IR spectrum of **1** is a strong, sharp band at 2208 cm^{-1}, which we attribute to the iridium-hydrogen stretching mode. The high value of ν_{Ir-H} suggests that the hydrido ligand is trans to the chloro ligand.[51] We had initially reported[36] that the spectrum also exhibits a band at 245 cm^{-1}, which we ascribed to ν_{Ir-Cl} and took to be support for trans H-Cl stereochemistry.[52] We now find that the 245-cm^{-1} band is actually an instrumental artifact and we have been unable to locate unequivocally a ν_{Ir-Cl} band. Either this band is of low intensity or the Ir-Cl bond is particularly weak, causing ν_{Ir-Cl} to fall below 230 cm^{-1}.

The low-field region of the ^1H NMR spectrum of **1** consists of a broad area of aromatic resonances and a series of multiplets consistent with an η^3-allyl moiety.[53] The details of this spectrum are compiled in Table I. The assignments therein have been confirmed by homonuclear decoupling and comparison with the literature.[54] The observation of a set of resonances in the high-field region confirms the presence of a hydrido ligand and the doublet of doublets pattern with $^2J_{HP}$ values of 13.8 and 16.2 Hz indicates that the two P nuclei are



I

Table III. Positional and Thermal Parameters for the Nongroup Atoms of $IrClH(\eta^3\text{-}C_3H_4(1\text{-}Ph))(PPh_3)_2$

ATOM	X[A]	Y	Z	B11[B] OR B, A^2	B22	B33	B12	B13	B23
IR	0.127301(13)	1/4	0.506218(8)	31.70(11)	45.30(26)	10.38(5)	-2.07(18)	0.61(4)	0.46(19)
CL	0.17615(11)	0.02981(17)	0.51926(7)	52.7(8)	42.9(13)	14.64(25)	-0.8(8)	0.16(38)	4.01(49)
P(1)	0.25428(10)	0.30228(19)	0.56033(7)	33.6(6)	53.0(13)	12.92(26)	2.1(8)	-1.67(32)	0.8(5)
P(2)	0.17129(10)	0.29687(18)	0.41052(6)	37.2(6)	46.5(13)	10.98(24)	-0.6(7)	2.33(31)	0.75(43)
C(1)	0.0001(6)	0.1667(9)	0.47850(35)	45.3(32)	65.(8)	13.8(12)	-14.7(42)	-3.8(17)	0.4(25)
C(2)	-0.01492(38)	0.2383(8)	0.52792(28)	31.3(22)	61.(8)	15.3(11)	-4.7(37)	2.9(12)	5.8(25)
C(3)	0.03033(44)	0.2147(7)	0.58259(28)	38.2(27)	57.(7)	13.1(11)	-9.0(31)	3.9(14)	-3.0(19)
H	0.105(5)	0.380(9)	0.5018(27)	2.7(16)					
H1C(1)	0.008(8)	0.096(12)	0.4871(46)	3.3(31)					
H2C(1)	-0.027(6)	0.182(8)	0.4435(41)	5.2(21)					
HC(2)	-0.0458(38)	0.315(6)	0.5252(27)	1.4(11)					
HC(3)	0.046(6)	0.129(9)	0.5892(41)	0.8(24)					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table IV. Derived Parameters for the Rigid Group Atoms of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
C1R1P1	0.36243(27)	0.28303(50)	0.52244(23)	3.52(12)	C4R1P2	-0.07312(23)	0.41424(48)	0.34443(19)	3.83(13)
C2R1P1	0.37213(30)	0.18582(46)	0.48315(26)	4.17(15)	C5R1P2	0.01085(29)	0.33490(50)	0.26102(14)	3.85(13)
C3R1P1	0.43357(37)	0.36321(48)	0.53155(25)	4.64(16)	C6R1P2	-0.06639(25)	0.3896(5)	0.28366(19)	4.27(14)
C4R1P1	0.45298(37)	0.1688(5)	0.45297(25)	4.86(17)	C1R2P2	0.23130(29)	0.18448(39)	0.36601(19)	3.00(10)
C5R1P1	0.51441(32)	0.3462(6)	0.50135(30)	5.60(27)	C2R2P2	0.20239(27)	0.06465(44)	0.37194(19)	3.60(12)
C6R1P1	0.52412(29)	0.2490(7)	0.46207(27)	6.00(18)	C3R2P2	0.29753(32)	0.21361(36)	0.32450(23)	4.43(15)
C1R2P1	0.26040(31)	0.45829(35)	0.58962(20)	3.02(10)	C4R2P2	0.23969(34)	-0.02605(35)	0.33635(23)	4.33(14)
C2R2P1	0.30365(32)	0.48279(42)	0.64339(19)	4.16(14)	C5R2P2	0.33483(31)	0.12291(49)	0.28891(21)	4.88(17)
C3R2P1	0.22288(30)	0.55286(45)	0.55565(17)	3.58(12)	C6R2P2	0.30592(34)	0.00308(43)	0.29484(22)	4.68(16)
C4R2P1	0.30938(34)	0.60187(49)	0.66418(18)	4.84(16)	C1R3P2	0.23310(29)	0.44158(36)	0.40343(21)	2.91(10)
C5R2P1	0.22852(34)	0.67193(39)	0.57745(22)	4.40(15)	C2R3P2	0.18320(22)	0.54864(47)	0.40148(23)	4.01(13)
C6R2P1	0.27187(37)	0.69644(37)	0.63121(24)	4.76(16)	C3R3P2	0.32661(29)	0.44659(39)	0.40497(24)	3.96(13)
C1R3P1	0.27054(33)	0.20842(47)	0.62733(18)	3.48(12)	C4R3P2	0.22680(34)	0.66070(37)	0.40107(26)	4.50(15)
C2R3P1	0.33283(35)	0.1139(5)	0.62770(21)	4.67(16)	C5R3P2	0.37021(22)	0.5586(5)	0.40456(28)	5.17(19)
C3R3P1	0.21905(29)	0.23197(45)	0.67790(22)	3.96(13)	C6R3P2	0.32030(35)	0.66569(38)	0.40261(28)	4.96(17)
C4R3P1	0.34363(37)	0.04293(48)	0.67864(27)	5.33(22)	C1RALL	0.01340(27)	0.29132(40)	0.63571(15)	3.03(10)
C5R3P1	0.22984(35)	0.1610(6)	0.72884(18)	4.88(17)	C2RALL	-0.01034(31)	0.23566(34)	0.68924(20)	4.03(13)
C6R3P1	0.29213(41)	0.0665(5)	0.72922(21)	5.51(19)	C3RALL	0.02127(28)	0.41736(41)	0.63274(16)	3.41(12)
C1R1P2	0.07462(22)	0.32959(46)	0.35991(16)	2.73(9)	C4RALL	-0.02620(31)	0.30603(48)	0.73980(15)	4.76(15)
C2R1P2	-0.00262(27)	0.38425(47)	0.38255(14)	3.15(11)	C5RALL	0.00541(33)	0.48773(34)	0.68330(22)	4.07(14)
C3R1P2	0.08135(23)	0.30491(47)	0.29915(17)	3.42(11)	C6RALL	-0.01832(32)	0.43207(46)	0.73683(17)	4.62(15)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
R1P1	0.44327(24)	0.26601(39)	0.49226(17)	-0.4381(37)	-2.6751(38)	2.5664(40)
R2P1	0.26613(20)	0.57736(34)	0.61042(15)	1.0006(47)	2.2040(30)	-2.5403(49)
R3P1	0.28134(23)	0.13745(36)	0.67827(16)	0.9165(41)	-2.6562(30)	-1.1869(40)
R1P2	0.00412(18)	0.35958(31)	0.32179(13)	-2.1805(48)	2.2546(23)	1.8102(47)
R2P2	0.26861(20)	0.09378(34)	0.33042(14)	-0.7126(32)	2.6850(30)	2.4494(33)
R3P2	0.27670(22)	0.55364(33)	0.40302(13)	-2.0551(29)	-3.1091(35)	0.0066(34)
RALL	-0.00246(17)	0.36170(34)	0.68627(13)	-0.2311(34)	2.5888(26)	-1.2743(30)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA (RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

nonequivalent and both cis to the hydrido ligand.[55] The nonequivalence of the phosphorus nuclei in **1** is substantiated by its $^{31}P\{^1H\}$ NMR spectrum, which consists of an AB quartet (Table I). The small value of $^2J_{PP}$, 5.0 Hz, indicates that the phosphine ligands occupy mutually cis positions. The combined results of these stereochemical indicators suggest that the structure of **1** corresponds to isomer I, which is corroborated by the solid-state structure discussed below.

Complex **1** is also obtained in improved yields from the reactions of allylbenzene or *trans*-β-methylstyrene with *trans*-$IrCl(N_2)(PPh_3)_2$. In each case the product arises from oxidative addition of an Ir(I) center to an allylic C-H bond. Presumably this insertion is preceded by the formation of an Ir(I)-olefin complex. In these intermediate complexes the allylic C-H bonds are held in proximity to the metal center by olefin coordination. The need for such a juxtaposition has been well documented.[37] The formation of complex **1** from these olefins lends credence to the proposed allyl metal hydride mechanism for metal-catalyzed olefin isomerizations, as these coordination and oxidative addition steps are entirely analogous to the initial portion of this mechanism as depicted in Scheme II. At the time of our initial observation of these reactions the formation of $MoH(\eta^3\text{-}C_3H_5)(dppe)_2$ by addition of a Mo center to propene was the only analogous reaction reported.[32] In the interim similar reactions of olefins with a Ru(0) complex have also appeared.[30,35]

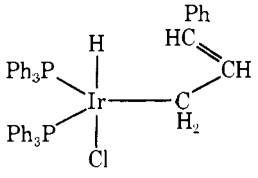
A more convenient iridium-containing starting material for the preparation of **1** is $[\text{IrCl(COT)}_2]_2$. Mixtures of PPh_3 (4 mol) and $[\text{IrCl(COT)}_2]_2$ (1 mol) are thought to contain monomeric "$\text{IrCl(PPh}_3)_2$",[42] possibly solvated, which is analogous to the reactive species generated by *trans*-$\text{IrCl(N}_2)(\text{PPh}_3)_2$.[38] The $[\text{IrCl(COT)}_2]_2$-PPh_3 mixture affords shorter reaction times as a result of increased solubility. Cleaner products in enhanced yields are also obtained as *trans*-$\text{IrCl(N}_2)(\text{PPh}_3)_2$ invariably contains *trans*-$\text{IrCl(CO)(PPh}_3)_2$ as a contaminant not found in carefully prepared samples derived from $[\text{IrCl(COT)}_2]_2$. Thus phenylcyclopropane, allylbenzene, and *trans*-β-methylstyrene each react with "$\text{IrCl(PPh}_3)_2$" generated in situ to form **1** in high yield. Use of $[\text{IrCl(COT)}_2]_2$ also allows the introduction of donor ligands other than PPh_3, whereas the dinitrogen complex can be satisfactorily obtained only with this phosphine. Thus we have also prepared complexes **2–5**, in which AsPh_3, SbPh_3, $\text{P}(p\text{-Tol})_3$, or $\text{As}(p\text{-Tol})_3$ are substituted for PPh_3 in **1** by the reaction of $[\text{IrCl(COT)}_2]_2$ with allylbenzene and the appropriate ligand. The similarity of the IR and NMR spectra of these complexes with those of **1** suggests that they also adopt geometry I. Attempts to prepare additional A-M-H complexes using PEt_3, PMe_2Ph, PMePh_2, $\text{P}(o\text{-Tol})_3$, dppe, or P(OPh)_3 as ligands were unsuccessful.

In the course of these synthetic reactions we routinely monitored the residual substrate to ascertain the extent of any isomerization. Although no attempt has been made to quantify these isomerizations, the general trends are interesting. The reactions of allylbenzene with *trans*-$\text{IrCl(N}_2)(\text{PPh}_3)_2$ or "$\text{IrCl(PPh}_3)_2$" both yield substrate which has been isomerized to β-methylstyrene to the extent of approximately 20 ± 5%. The analogous reactions with β-methylstyrene produce no observable isomerization. This is not surprising as the equilibrium concentation of the terminal olefin, allylbenzene, is only 0.05% at 25 °C.[56] The extent of isomerization of allylbenzene is very dependent on L in the "IrClL_2" systems, increasing as the basicity of L decreases. When L is the highly basic PEt_3 no isomerization is observed even after 1 week. The activity of the system increases as the ligands become less basic[57] in the order $\text{PMe}_2\text{Ph} < \text{PMePh}_2 < \text{PPh}_3$. With the weakly basic ligand P(OPh)_3 complete conversion of allylbenzene to β-methylstyrene is rapidly achieved. Ligands such as P(OPh)_3 lower the electron density at the metal center thereby stabilizing the lower formal oxidation state. This should promote the reductive elimination of hydrido and allyl ligands from an intermediate A-M-H complex and facilitate the isomerization if this reductive elimination is the rate-determining step. Highly basic ligands such as PEt_3 decrease the effective oxidative state of the iridium center in "IrClL_2" and thus favor both olefin coordination and oxidative addition while preventing reductive elimination. That discrete A-M-H complexes are not obtained with these alkyl phosphines may result from interactions between the metal and C-H bonds of the ligands, as has been previously demonstrated.[58] We have noted[36] that no β-methylstyrene or allylbenzene is observed in the preparation of complex **1** from *trans*-$\text{IrCl(N}_2)(\text{PPh}_3)_2$ and phenylcyclopropane. This is also the case when "$\text{IrCl(PPh}_3)_2$" is used. The facile formation of **1** from either olefin suggests that the complex possesses high stability and that any small concentration of olefin would be quickly scavenged by "$\text{IrCl(PPh}_3)_2$".

The thermodynamic stability of **1** is consistent with its lack of catalytic activity. Mixtures of complex **1** (1 mol) and allylbenzene (100 mol) in deuteriochloroform showed no production of β-methylstyrene over the course of 10 weeks at 40 °C, as judged by ^{1}H NMR spectroscopy. Reductive elimination of the hydrido and allyl ligand appears to be unfavorable. This is substantiated by the variable temperature (−60 to 60 °C) ^{1}H and ^{31}P NMR spectra of **1–5**, which indicate that no dynamic equilibria with corresponding Ir(I)-olefin complexes take place, in contrast to the results observed with $\text{NiH}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)$[31] and $\text{MoH}(\eta^3\text{-C}_3\text{H}_5)(\text{dppe})_2$.[32]

When heated at 60 °C for prolonged periods complex **1** does slowly decompose to yield β-methylstyrene. This olefin is also produced in the reactions of CO or PF_3 with **1**. No such reaction takes place between **1** and propene (1 atm) or triphenylphosphine. Here the stronger π-bonding ligands stabilize the metal in the +1 oxidation state, as *trans*-$\text{IrCl(CO)(PPh}_3)_2$ and *trans*-$\text{IrCl(PF}_3)(\text{PPh}_3)_2$, respectively, and thereby facilitate reductive elimination of olefin from **1**. Solutions of **1** in chloroform are very slowly decomposed by dioxygen, again yielding β-methylstyrene. In none of the reactions is the production of allylbenzene observed. The direction of these processes suggests that if the η^3-allyliridium(III) hydride complex were less stable it could serve as a good catalyst for the isomerization of primary to internal olefins, as depicted in Scheme II.

Treatment of complex **1** with HCl (1 atm) at 25 °C produces both β-methylstyrene and allylbenzene in approximately equivalent amounts. This result, in contrast to the formation of only the former, thermodynamically favored olefin in the reaction of **1** with CO or PF_3, indicates that the HCl reaction is kinetically controlled. A similar result has been reported by Nixon and Wilkins[34] for the reactions of $\text{Rh}(\eta^3\text{-allyl})(\text{PF}_3)_3$ complexes with HCl. At −75 °C the intermediate complex $\text{RhClH}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)_2$ is observed but it decomposes to yield propene on warming. In those cases involving asymmetric η^3-allyl ligands, roughly 1/1 mixtures of the two possible olefins are observed, regardless of the nature of the allyl substituents. These results clearly indicate that the formation of olefin does not proceed in the expected manner, i.e., by reductive coupling of hydrido and η^1-allyl ligands in a complex analogous to II. The most stable η^1-allyl group corresponds to the thermodynamically favored olefin and it is initial rearrangement (η^3- → η^1-allyl) which directs the course of the reaction. A number of mechanistic pathways, including outer-sphere protonation of the η^3-allyl group, are conceivable but labeling studies are required to discriminate among these.

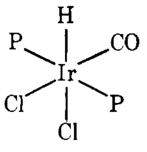


II

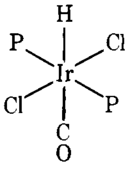
Two hydride complexes are also formed in the reaction of HCl with **1**, as judged by the high-field ^{1}H NMR spectrum of the iridium-containing product. Two hydride signals are present, again of approximately equivalent intensity, as binomial triplets with H-P coupling constants of about 20 Hz. Thus in both species the hydrido ligand is cis to two equivalent phosphine ligands. The absence of H-H coupling indicates that the signals arise from different species rather than from a single dihydride complex. The IR spectrum of this mixture contains a broad band centered at 2260 cm^{-1} which we attribute to $\nu_{\text{Ir-H}}$. These results suggest that this reaction proceeds as in eq 5. Complexes of stoichiometry $\text{IrCl}_2\text{H(PPh}_3)_2$ have also

$$\text{IrClH}[\eta^3\text{-C}_3\text{H}_4(1\text{-Ph})](\text{PPh}_3)_2 + \text{HCl} \longrightarrow \begin{matrix}[\text{PhCH=CHCH}_3 + \alpha\text{-IrCl}_2\text{H(PPh}_3)_2] \\ + \\ [\text{PhCH}_2\text{CH=CH}_2 + \beta\text{-IrCl}_2\text{H(PPh}_3)_2]\end{matrix} \quad (5)$$

been reported as the products of the reactions of $\text{IrH}_3(\text{PPh}_3)_2$[59] or *trans*-$\text{IrCl(N}_2)(\text{PPh}_3)_2$[60,61] with HCl. These previously reported complexes react with CO to produce compounds of stoichiometry $\text{IrCl}_2\text{H(CO)(PPh}_3)_2$ whose stereochemistries have been assigned as III[61] and IV,[62] where P represents triphenylphosphine.



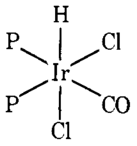
III



IV

	III	IV
ν_{Ir-H}	2240 cm^{-1}	2154 cm^{-1}
ν_{CO}	2024	2003
ν_{Ir-Cl}	313,265	320

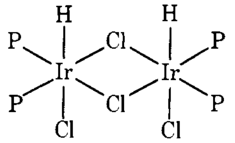
Vaska[62] reported that the HCl adduct of *trans*-IrCl(CO)(PPh$_3$)$_2$ also adopts structure III. These structural assignments are based upon the empirical rules for ν_{Ir-H} and ν_{Ir-Cl} outlined by Chatt et al.[51] and Jenkins and Shaw.[52] Thus in III, the high value of ν_{Ir-H} and the low value of ν_{Ir-Cl} indicate that the Cl and H ligands are mutually trans while the remaining value of ν_{Ir-Cl}, 313 cm^{-1}, is in the region for Cl trans to CO. For IV the decreased value of ν_{Ir-H} suggests that the hydrido ligand is not trans to a halide while the single high value of ν_{Ir-Cl} at 320 cm^{-1} is consistent with mutually trans chloro ligands. Structure IV is further supported by the observation of H-CO vibrational interaction.[63] The IrCl$_2$H(PPh$_3$)$_2$ mixture obtained from **1** and HCl reacts with CO to yield a single complex of stoichiometry IrCl$_2$H(CO)(PPh$_3$)$_2$ unlike either III or IV. Thus neither α- nor β-IrCl$_2$H(PPh$_3$)$_2$ is equivalent to those complexes previously reported. The IR spectrum of the new complex exhibits bands at 2245, 2075, 300, and 260 cm^{-1} which we attribute to ν_{Ir-H}, ν_{CO}, and ν_{Ir-Cl}(2), respectively. The high value for ν_{Ir-H} in conjunction with the low value of ν_{Ir-Cl} at 260 cm^{-1} again suggest a trans H-Ir-Cl array. Of the six possible octahedral isomers of IrCl$_2$H(CO)(PPh$_3$)$_2$ four are thus eliminated, leaving only structures III and V. The ν_{CO} and remaining ν_{Ir-Cl} values of the new complex are clearly dissimilar to those reported by Vaska[62] for III. Thus the new complex probably adopts structure V, although ν_{Ir-Cl} at 300 cm^{-1} is at slightly higher energy than is usually observed when Cl and PR$_3$ ligands are trans.[52] In the new complex the increased value of ν_{CO} with respect to that of III is consistent with a trans P-CO stereochemistry, as the π acidity of the phosphine ligand allows it to complete more successfully for electron density than the Cl ligand thereby decreasing the back-donation to CO. The low solubility of these complexes prohibits further comparisons based on ^{1}H and ^{31}P NMR spectra. The novel feature of structure V is the cis coordination of the phosphine ligands. A trans arrangement for these bulky groups, as in III, should be favored on steric grounds. This is consistent with the observation that upon standing in benzene or acetone at room temperature V slowly isomerizes to III, as verified by comparison with an authentic sample.[62]



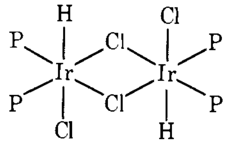
V

In order to determine the stereochemical course of the reaction of HCl with **1**, we substituted HBr to ascertain which Cl ligand in V is retained from **1**. Subsequent treatment with CO produced a complex which contained no chlorine as determined by the absence of ν_{Ir-Cl} bands in its IR spectrum. This was verified by elemental analysis. Other bands in the IR spectrum at 2240 and 2070 cm^{-1}, ν_{Ir-H} and ν_{CO}, respectively, suggest that the complex is IrBr$_2$H(CO)(PPh$_3$)$_2$ with a structure analogous to V. The facile replacement of the Cl ligand from **1** is presumably a result of the trans labilization of the hydrido ligand.

The formation of two products of apparent stoichiometry IrCl$_2$H(PPh$_3$)$_2$ from the reaction of **1** with HCl is unusual. Recently a number of five-coordinate Ir(III) complexes have been prepared.[61,64-66] The stability of the complexes requires the presence of a ligand of high trans influence, such as the hydride here. Although no structural reports have appeared, these complexes are proposed, by analogy with two similar rhodium complexes, RhI$_2$(CH$_3$)(PPh$_3$)$_2$[67] and RhCl$_2$H[P(n-Pr)$_2$(t-Bu)]$_2$,[68] to adopt square-pyramidal geometries with the ligand of highest trans influence occupying the apical site. This is substantiated by the observation[61,64,66] that addition of a nucleophile occurs trans to the ligand of highest trans influence, which would correspond to attack at the open coordination site below the basal plane. Our results are not readily accommodated within this scheme. The ^{1}H NMR spectrum of the IrCl$_2$H(PPh$_3$)$_2$ mixture indicates that the hydride complexes each contain equivalent phosphines in positions cis to the hydrido ligand. The reaction of CO clearly does not proceed by addition trans to the hydride, the ligand of highest trans influence, and the retention of cis phosphine ligands in the CO adduct strongly suggests that these ligands are also cis in the IrCl$_2$H(PPh$_3$)$_2$ complexes. These results are incompatible with square-pyramidal structures for the IrCl$_2$H(PPh$_3$)$_2$ complexes. One possible explanation is that the IrCl$_2$H(PPh$_3$)$_2$ mixture contains dimeric rather than monomeric complexes. The two complexes would then be VI and VII. In each complex the phosphine ligands are in the correct environment and addition of CO will cleave one of the bridge bonds affording the carbonyl adduct observed. This explanation is supported by the pale yellow color of the IrCl$_2$H(PPh$_3$)$_2$ mixture. Five-coordinate Ir(III) complexes generally are intensely colored.[64] In contrast to these results the HCl adduct of *trans*-IrCl(N$_2$)(PPh$_3$)$_2$ conforms to the criteria for a true five-coordinated species. The trans phosphine ligands in this complex require that in a dimer such as VI or VII the hydrido ligand be trans to a chloro ligand and thus the trans bond weakening effect of the hydrido ligand would retard dimer formation. A more complete elucidation of these results must await further study.



VI



VII

Description of the Crystal and Molecular Structure of IrClH[η^3-C$_3$H$_4$(1-Ph)](PPh$_3$)$_2$ (1). The crystal structure of **1** consists of four well-separated molecules with a closest intermolecular H···H approach of 2.24 Å. A stereoscopic packing diagram is shown in Figure 1 while Figure 2 presents a stereoview of the molecule. Intramolecular distances and angles are compiled in Table VII.

The inner coordination sphere is depicted in Figure 3, which also contains atom labels and selected bond distances. The observed structure is in accord with that predicted from spectroscopic data. The coordination geometry is pseudooctahedral with cis phosphine ligands and an η^3-allyl moiety which occupies two coordination sites. The Ir-P bond lengths are normal. The small difference between these values is presumably a result of the differing trans influences of the C(1) and C(3) extremes of the allyl group. The Ir-C(1) bond is stronger than that of Ir-C(3), as judged by the Ir-C distances, and thus exerts a stronger trans influence, thereby causing Ir-P(1) to be longer than Ir-P(2).

The hydride hydrogen atom was easily located and readily refined to a chemically reasonable position. The H-Ir-Cl angle

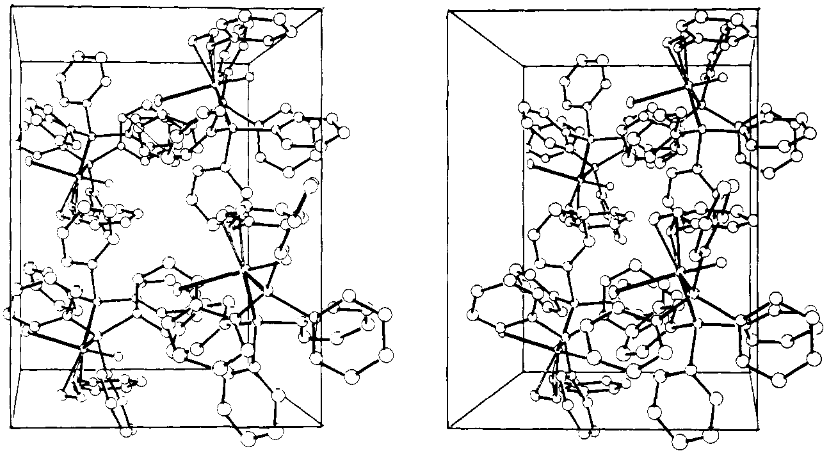


Figure 1. A stereoview of the unit cell of **1**, $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$. Phenyl and allylic hydrogen atoms have been omitted for clarity. The *x* axis is vertical from bottom to top, the *y* axis is horizontal to the right, and the *z* axis is perpendicular to the paper going away from the reader. The vibrational ellipsoids are drawn at the 20% level here and in the following figure.

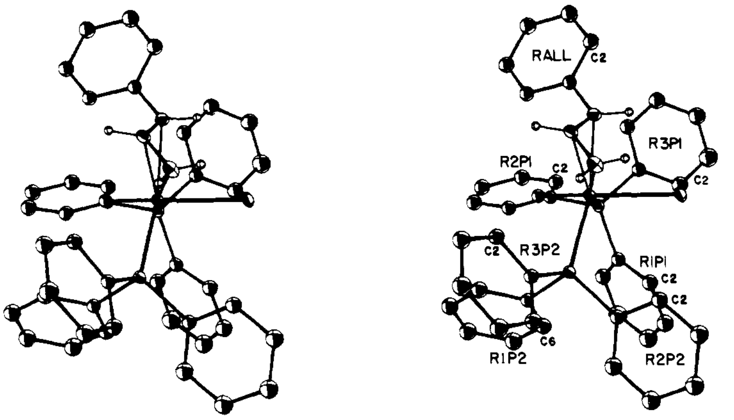


Figure 2. A stereoview of the overall molecule of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$. Phenyl hydrogen atoms have been omitted for clarity. A portion of the labeling scheme is included.

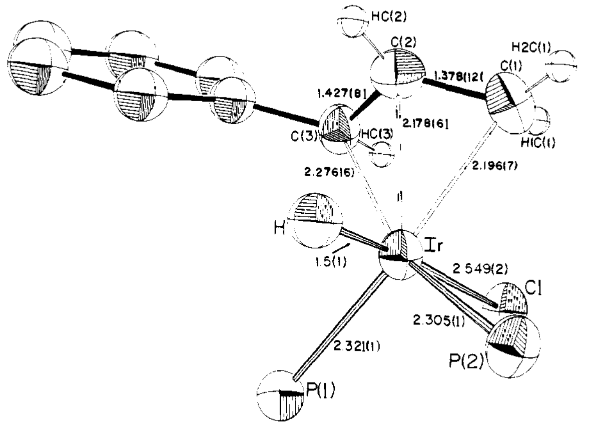


Figure 3. A perspective view of the inner coordination sphere of $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$. The numbering scheme and selected distances are shown. The vibrational ellipsoids are drawn at the 50% level.

of 176 (3)° is consistent with the spectroscopic prediction of trans H and Cl ligands. The Ir–H distance, 1.5 (1) Å, may be somewhat shorter than that observed in other Ir(III) hydride complexes[69,70] and transition-metal hydrides in general, approximately 1.7 Å.[71] This short bond length may reflect the weak trans influence of the chloro ligand as does the high value of ν_{Ir-H}.[51]

The Ir–Cl bond is extremely long, 2.549 (2) Å, presumably as a result of the trans influence of the strongly bound hydrido ligand. Iridium(III)-chlorine bond distances from 2.33 to 2.51 Å have been found.[72–86] We believe that this bond in **1** is the longest of its kind reported. A longer terminal Ir–Cl distance, 2.599 Å, has been determined only for the five-coordinate Ir(I) complex $IrCl(C_8H_{12})(Ph_2PCH_2(C_5H_8O_2)CH_2PPh_2)$.[87] The lability of the Cl ligand in **1**, as shown by its facile substitution by the Br^- ion, is consistent with this long bond.

Considerable use has been made of iridium-chlorine stretching frequencies to diagnose the trans bond weakening effect of ligands in octahedral d^6 Ir(III) complexes. Values of ν_{Ir-Cl} decrease for trans ligands in the order Cl^-, CO, PR_3, alkyl$^-$ or aryl$^-$, H^-.[52,62,65] A similar correlation with ν_{Ru-Cl} has been demonstrated for Ru(II)–Cl systems[88] and we have recently shown[89] that the Ru–Cl bond length can also be used as an indicator of the trans influence of a ligand. The Ir(III)–Cl bond lengths may be used similarly. Table VIII contains a comparison of iridium-chlorine stretching frequencies and bond lengths and shows that, as expected, the bond length increases as the value of ν_{Ir-Cl} decreases.

The geometry and dimensions of the allyl group in **1** are normal. The C(1)–C(2)–C(3) angle, 120.8 (8)°, is as expected for an sp^2-hybridized carbon center and the dihedral angle between the planes defined by the three carbon atoms of the allyl group and C(1), Ir, and C(3), 73.1 (8)°, is consistent with that found in other η^3-allyl complexes, 70–80°.[90] Useful comparisons can be made between the structures of **1** and another octahedral Ir(III) η^3-allyl complex, $[IrCl(\eta^3\text{-}C_3H_5)(CO)(PMe_2Ph)_2][PF_6]$[76] (**6**). As is characteristic of η^3-allyl complexes the metal-carbon (central) distances, 2.178 (6) and 2.24 (1) Å, in complexes **1** and **6**, respectively, are shorter than the respective metal-carbon (terminal) distances.

Table VII. Selected Distances (Å) and Angles (deg) in $IrClH[\eta^3\text{-}C_3H_4(1\text{-}Ph)](PPh_3)_2$

		Bond Distances	
Ir-Cl	2.549 (2)	C(1)-H1C(1)	0.81 (13)
Ir-P(1)	2.321 (1)	C(1)-H2C(1)	0.90 (9)
Ir-P(2)	2.305 (1)	C(2)-HC(2)	0.96 (7)
Ir-C(1)	2.196 (7)	C(3)-HC(3)	0.98 (10)
Ir-C(2)	2.178 (6)	P(1)-C(1)R(1)P(1)	1.835 (5)
Ir-C(3)	2.276 (6)	P(1)-C(1)R(2)P(1)	1.843 (4)
Ir-H	1.5 (1)	P(1)-C(1)R(3)P(1)	1.842 (5)
C(1)-C(2)	1.378 (12)	P(2)-C(1)R(1)P(2)	1.870 (4)
C(2)-C(3)	1.427 (8)	P(2)-C(1)R(2)P(2)	1.825 (5)
C(3)-C(1)Ph	1.483 (8)	P(2)-C(1)R(3)P(2)	1.848 (5)
		Nonbonded Distances	
Ir-H1C(1)	2.49 (12)	Ir-HC(2)	2.71 (8)
Ir-H2C(1)	2.80 (10)	Ir-HC(3)	2.59 (9)
H-C(2)	2.44 (9)		
		Bond Angles	
Cl-Ir-P(1)	86.7 (1)	C(1)-Ir-C(2)	36.7 (3)
Cl-Ir-P(2)	103.8 (1)	C(1)-Ir-C(3)	66.1 (3)
Cl-Ir-C(1)	83.2 (3)	C(2)-Ir-C(3)	37.3 (2)
Cl-Ir-C(2)	101.3 (2)	C(1)-C(2)-C(3)	120.8 (8)
Cl-Ir-C(3)	86.1 (2)	C(1)-C(2)-HC(2)	122 (4)
Cl-Ir-H	176 (3)	C(2)-C(1)-H1C(1)	112 (8)
P(1)-Ir-P(2)	101.6 (1)	C(2)-C(1)-H2C(1)	122 (6)
P(1)-Ir-C(1)	162.9 (2)	H1C(1)-C(1)-H2C(1)	117 (9)
P(1)-Ir-C(2)	133.7 (2)	C(3)-C(2)-HC(2)	116 (4)
P(1)-Ir-C(3)	99.5 (2)	C(2)-C(3)-C(1)Ph	120.6 (6)
P(1)-Ir-H	89 (3)	C(2)-C(3)-HC(3)	115 (5)
P(2)-Ir-C(1)	94.3 (2)	C(1)Ph-C(3)-HC(3)	118 (5)
P(2)-Ir-C(2)	119.8 (2)	C(1)R(1)P(1)-P(1)-C(1)R(2)P(1)	103.3 (2)
P(2)-Ir-C(3)	157.1 (2)	C(1)R(1)P(1)-P(1)-C(1)R(3)P(1)	101.4 (2)
P(2)-Ir-H	78 (2)	C(1)R(2)P(1)-P(1)-C(1)R(3)P(1)	103.0 (2)
C(1)-Ir-H	101 (3)	C(1)R(1)P(2)-P(2)-C(1)R(2)P(2)	100.1 (2)
C(2)-Ir-H	81 (3)	C(1)R(1)P(2)-P(2)-C(1)R(3)P(2)	99.5 (2)
C(3)-Ir-H	94 (3)	C(1)R(2)P(2)-P(2)-C(1)R(3)P(2)	107.1 (2)
		Interplanar Angles	
[Ir, P(1), P(2)]-[C(1), C(2), C(3)]	74.7 (7)		
[Ir, C(1), C(3)]-[C(1), C(2), C(3)]	73.1 (8)		
[C(1), C(2), C(3)]-[C(1)Ph-C(6)Ph]	52.6 (7)		
[C(1), C(2), C(3)]-[H1C(1), C(1), H2C(1)]	144 (10)		
[C(1), C(2), C(3)]-[HC(3), C(3), C(1)Ph]	30 (6)		

However, in complex **1** there is an additional asymmetry, as the Ir-C(3) distance, 2.276 (8) Å, is significantly longer than that of Ir-C(1), 2.196 (7) Å.[76] Complex **1** also exhibits an asymmetry in the C-C bonds of the allyl group (C(1)-C(2) = 1.378 (12), C(2)-C(3) = 1.427 (8) Å); these have equivalent values of 1.38 (3) and 1.40 (3) Å in complex **6**. The long bonds in **1** involve C(3) and presumably result from phenyl substitution. However, there is little conjugation between allyl and phenyl groups, as indicated by a dihedral angle of 52.6 (7)° and C(3)-C(1)Ph[91] distance of 1.483 (8) Å. These structural variations do not reflect the incipient formation of an η^1-(σ)allyl complex such as **II**. Unlike the observed results, the C(2)-C(3) bond length in such a complex would be shorter than that of C(1)-C(2). This is also consistent with the lack of dynamic equilibria in **1**. In contrast, note that the bond-length variations in **6**, although only possibly significant, are consistent with the incipient formation of an η^1-allyl group and that this process readily occurs.[76] The bonding parameters are generally consistent with the η^3-allyl group of **1** being bound more strongly than that of **6**.

In conjunction with the structural determination of complex **6** we have described a set of parameters which facilitate comparisons between the geometries of η^3-allyl complexes.[76] Although these parameters were designed to deal only with unsubstituted η^3-allyl systems, their values for complex **1** are consistent with the observed trends. The value of *D*, the distance from Ir to the center of mass *O* of the C_3 allyl group, for **1**, 1.95 Å, is in accord with those found in other d^6 complexes; e.g., the complex $Ru(\eta^3\text{-}C_3H_5)_2(PPh_3)_2{\cdot}C_7H_8$[92] has a value of 1.94 Å for each allyl group. Similarly, a comparison of the values of *D* and the C(1)-C(2)-C(3) angle for **1** shows that **1** falls exactly on the least-squares line generated for other d^6 complexes. Consistent with the β angles of 90-93° found in other η^3-allyl complexes, the value of β, the angle between the Ir-*O* and the C(1)-C(3) vectors, in **1** is 91.9°.

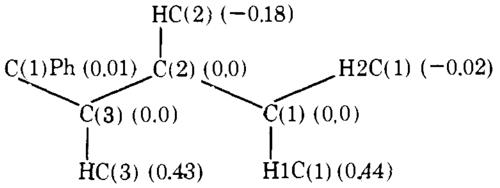
Table VIII. Iridium-Chlorine Stretching Frequencies and Bond Lengths in Octahedral Ir(III) Complexes

trans ligand	$\nu_{Ir\text{-}Cl}$, cm^{-1} [a]	Ir-Cl, Å
Cl^-	310-330	2.33-2.36[b]
CO	300-315	2.37-2.41[c]
PR_3	265-280	2.42[d]
alkyl$^-$ or aryl$^-$	250-260	2.44-2.51[e]
H^-	245-250	2.549[f]

[a] References 52, 62, and 65. [b] References 72 and 73. [c] References 74-79. [d] Reference 80. [e] References 74 and 81-86. [f] This work.

The orientation of the allyl group is such that atom C(2) is closer to the hydrido than to the chloro ligand. Earlier[36] we pointed out a close contact between atoms C(2) and H (Table VII) and suggested a potential decomposition pathway which could directly produce an iridium metallocyclobutane complex by hydride migration to atom C(2). Subsequent reductive C-C coupling would then yield phenylcyclopropane. As discussed above, only β-methylstyrene or allylbenzene, produced by hydride transfer to a terminal carbon atom, have been observed. This lack of cyclopropane formation is consistent with symmetry restrictions recently outlined by Mingos.[93]

The positions of the hydrogen atoms of the allyl group are of interest as we know of only one other complex, $V(\eta^3\text{-}C_3H_5)(CO)_3(dppe)$[90] (7), for which these atoms have been refined. The bond angles of the allyl group, ranging from 112 to 122° (av 119°), are as expected for sp^2-hybridized carbon atoms. However, there are deviations from ideal geometry as the planes H1C(1)-C(1)-H2C(1) and HC(3)-C(3)-C(1) Ph form angles of 36 (10) and 30 (6)° with the C(1)-C(2)-C(3) planes. Similar values of 26 and 27° were found in complex **7**.[90] The C(1)Ph and four hydrogen atoms deviate (Å) from the allyl plane as follows.



Errors in these displacements are approximately 0.1 Å. The Ir atom is displaced −1.79 Å in this scheme. The most striking feature is the bending of the anti protons, H1C(1) and HC(3), away from the metal. For complex **7** analogous displacements of 0.43 and 0.45 Å were reported.[90] The other displacements for complexes **1** and **7** are also similar. The syn protons of **7**, corresponding to H2C(1) and C(1)Ph, vary only 0.02 and −0.01 Å from the C(1)-C(2)-C(3) plane. Interestingly, in both **1** and **7** the hydrogen of the methine carbon atom, HC(2), is displaced toward the metal center, by −0.11 Å in **7**. Despite the bending back of the anti protons, close contacts exist between these atoms and the metal centers in both complexes **1** (Table VII) and **7**. Franke and Weiss[90] have suggested that this feature is responsible for the shielding experienced by these protons, a characteristic of the ^1H NMR spectra of η^3-allyl complexes.

Discussion

Recently the reactions of transiton-metal complexes with small-ring organic molecules have received intensive examination.[1] A common feature in many of these reactions is metal insertion into a three-membered ring to form a metallocycle, a number of which have been isolated.[9–17] A prerequisite for ring opening is the availability of two adjacent, vacant metal coordination sites. The complexes *trans*-$IrCl(N_2)(PPh_3)_2$, because of the lability of its N_2 ligand, and "$IrCl(PPh_3)_2$" are such precursors. Phenylcyclopropane does react with these complexes, but iridium metallocyclobutane complexes have not been forthcoming. The isolation instead of an η^3-allyl metal hydride complex, **1**, is readily explained by Scheme I and lends credence to this mechanism for cyclopropane isomerization. Although we have been unable to detect a transient metallocyclobutane complex, we believe that such a complex is initially formed by insertion of the iridium atom into the 1,2 bond of the cyclopropane. The complex then would rapidly undergo β-hydrogen abstraction to yield **1**, presumably by intermediate formation of an η^1-allyl complex such as II. Insertion into a bond adjacent to the phenyl ring is consistent with the preferred regioselectivity observed in all other metal-promoted phenylcyclopropane ring openings.[7,10,94–96] An earlier suggestion[15] that metal atom insertion occurs at the least substituted edge has recently been refuted by Puddephatt et al.[96] They have shown that platinum atom insertion into the 1,2 bond is kinetically controlled. The observed product, which corresponds to insertion into the 2,3 bond, is thermodynamically favored and results from rearrangement of the initially formed metallocycle. The preferential 1,2-bond cleavage of phenylcyclopropane probably arises from initial metal-aryl interaction which positions the cyclopropane near the metal center and thereby facilitates the opening of the adjacent bond. Here, as in a number of other cases,[3,94] the ring-opening reaction is promoted by the presence of phenyl substitution. This reactivity enhancement is presumably also a result of the initial metal-aryl interaction responsible for the direction of ring opening. Note, however, that, although unsubstituted cyclopropane does not react with *trans*-$IrCl(N_2)(PPh_3)_2$ or "$IrCl(PPh_3)_2$" under the conditions described here, an η^3-(C_3H_5) hydride complex analogous to **1** is formed using an alternative procedure.[97]

As described above, no β-methylstyrene, the olefin expected from reductive elimination of the hydrido and allyl ligands from **1**, is observed in the phenylcyclopropane reaction. This result is explained by the preferential interactions of the Ir(I) complexes with olefinic substrates. Thus any β-methylstyrene produced as in Scheme I would quickly be coordinated and **1** would be re-formed. Small amounts of α-methylstyrene have been observed. Unlike allylbenzene or β-methylstyrene this olefin does not react with *trans*-$IrCl(N_2)(PPh_3)_2$ or "$IrCl(PPh_3)_2$" under the conditions of the phenylcyclopropane reaction. Thus once produced α-methylstyrene will not be scavenged. This olefin presumably arises as in Scheme I from the 2-phenylallyl isomer of **1**. In fact this complex has been detected in small amounts. These observations are the subject of ongoing investigations.

The formation of **1** by apparent β-hydrogen abstraction from an initially formed iridium metallocyclobutane complex contrasts to the isolation of a number of these complexes. Although a similar facile abstraction of a cyano group from the β position in a series of oxygen-containing metallocyclobutanes has been observed,[98] hydrogen abstractions have not been observed in metallocycles formed in reactions of Pt,[10,11,15,16] Rh,[7,13,99,100] and Fe[14] complexes with cyclopropanes. In a number of these cases the formation of oligomeric products, involving μ-chloro ligands, blocks the vacant coordination site required for β-elimination[18] while in others the reaction is subject to stereochemical restraints, e.g., the production of anti-Bredt olefins.[5] The bulk of the ligands in the metallocyclobutane precursor to **1** may prevent dimerization. The iridium and β-hydrogen atoms in such a metallocycle would be in a syn-periplanar configuration, exactly that required for β-elimination.

The lack of catalytic olefin isomerization using complexes **1–5** presumably arises from their exceptional stability as octahedral Ir(III) complexes.[40] The strong bonding of the iridium atom to both hydrido and allyl ligands has already been noted. However, additional factors must also be important as we have recently synthesized other Ir(III) η^3-allyl hydride complexes from propene or cyclopropane, isobutene, and 1-butene or *trans*-2-butene[97] and find that the stability of these complexes is much less than that of **1–5**. The phenyl group of the allyl ligand in **1–5** may be the cause of their stability.

The formation of complexes **1–5** from allylbenzene and β-methylstyrene strongly supports the allyl metal hydride mechanism for olefin isomerizations (Scheme II). Although the complexes themselves do not act as catalysts in this reaction, their production of β-methylstyrene upon treatment with CO or PF_3 is in accord with the expected results of Scheme II, in that the thermodynamically favored internal olefin results. In complexes **1–5** strong ligands, such as CO or PF_3, are required to cause reductive elimination. On the other hand, in allyl metal hydride complexes in which the metal-hydride and metal-allyl bonding is not as strong as that in complexes **1–5**, this reductive elimination will more readily occur. Thus, a less efficient incoming ligand, for example, a terminal olefin, could be effective with less stable allyl metal hydride complexes. In this manner the catalytic cycle for converting terminal to internal olefins shown in Scheme II would result.

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Supplementary Material Available: Root-mean-square amplitudes of vibration (Table V), idealized positions for the phenyl hydrogen atoms (Table VI), and a listing of observed and calculated structure amplitudes (28 pages). Ordering information is given on any current masthead page.

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