Journal of Organometallic Chemistry, 272 (1984) 295–307
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FORMATION OF AN IRIDIUM σ-CYCLOPROPANE COMPLEX BY THE INTRAMOLECULAR ACTIVATION OF A CYCLOPROPYLPHOSPHINE: REARRANGEMENT TO A CHELATING σ-VINYL COMPLEX *

WILEY J. YOUNGS, BARBARA L. SIMMS, and JAMES A. IBERS
Department of Chemistry, Northwestern University, Evanston, IL 60201 (U.S.A.)

(Received March 6th, 1984)

Summary

When $(\text{t-Bu})_2PCH_2\overline{CHCH_2CH_2}$ is combined with $[IrCl(C_8H_{14})_2]_2$ in toluene, the σ-bound cyclopropane complexes $\overline{IrClH(P(\text{t-Bu})_2CH_2CHCH_2CH})(P(\text{t-Bu})_2CH_2\overline{CHCH_2CH_2})$ (**1a**, **1b**) are formed. Complexes **1a**,**1b** react readily with H_2 to form $IrClH_2(P(\text{t-Bu})_2CH_2\overline{CHCH_2CH_2})_2$ (**2**). In polar solvents **1a**,**1b** isomerize to the σ-vinyl chelated complex $\overline{IrClH(P(\text{t-Bu})_2CH_2C(CH_3)CH})(P(\text{t-Bu})_2CH_2\text{-}\overline{CHCH_2CH_2})$ (**3**). The structure of this 5-coordinate, 16-electron Ir^{III} complex was deduced from spectroscopic data, reaction chemistry, and from the crystal structure of its CO adduct (**4**). Compound **4** crystallizes in the monoclinic space group $C_{2h}^5\text{-}P2_1/n$ (a 15.610(14), b 15.763(16), c 11.973(13) Å, and β 104.74(5)°) with 4 molecules per unit cell. The final agreement indices for 2326 reflections having $F_o^2 > 3\sigma(F_o^2)$ are $R(F) = 0.089$ and $R_w(F) = 0.095$ (271 variables) while $R(F^2)$ is 0.148 for the 3423 unique data. Bond lengths in the 5-atom chelate ring $\overline{Ir\text{–}P\text{–}C\text{–}C{=}C}$ are Ir–P 2.341(4), P–C 1.857(26), C–C 1.520(30), C=C 1.341(25), and C–Ir 1.994(21) Å. The Ir–Cl distance is 2.479(5) Å.

Introduction

The activation of carbon–hydrogen and carbon–carbon bonds by soluble transition metal complexes is an important area of research in organometallic chemistry [1]. Since the initial reports of C–H bond activation, a number of examples of intramolecular C–H bond activation have been reported [2]. Intermolecular C–H

---

* Among his seminal contributions to chemistry Prof. Sei Otsuka has carried out an extensive series of studies of the interactions of bulky phosphines with transition metal systems and the resultant reactivity of such complexes. Thus, J.A.I. takes great pleasure in dedicating this paper to Sei Otsuka – a gentleman, a superb chemist, but most importantly a close friend.

0022-328X/84/$03.00

activation of saturated hydrocarbons with iridium complexes has been the subject of several recent papers [3].

Previously reported work of this and other research groups has shown that activation of cyclopropane rings by transition metal complexes generally results either in the cleavage of a C–C bond of the cyclopropane ring to form a metallacyclobutane or in the cleavage of a C–C bond and a C–H bond to form an allyl hydride [4]. We have previously reported the interaction of di-t-butyl(cyclopropylmethyl)phosphine, $P(t\text{-}Bu)_2CH_2CHCH_2CH_2$, with Pd^{II} and Pt^{II} to afford chelating σ-allyl complexes [5]. For the formation of these allyl systems we have not shown whether C–C or C–H bond activation occurs first.

We now report the intramolecular activation of a C–H bond of the cyclopropyl side chain of $P(t\text{-}Bu)_2CH_2CHCH_2CH_2$ by Ir^I to afford stable complexes in which there is a σ-bond between Ir and the cyclopropane moiety. We propose mechanisms for their formation and isomerization and discuss some of their reaction chemistry. Some of these results have appeared previously [6]. Subsequent to ref. 6 a report on the intermolecular activation of a C–H bond of cyclopropane to afford a σ-iridium-cyclopropyl complex has appeared [3b].

Experimental section

General remarks. All reactions were carried out under an atmosphere of prepurified nitrogen with the use of standard Schlenk-line techniques. Di-t-butyl(cyclopropylmethyl)phosphine was prepared as described previously [5]. Iridium trichloride hydrate was used as received from Johnson-Matthey, Inc. Solvents were purified by standard methods.

Elemental analyses were performed by Micro-Tech Laboratories, Skokie, IL or by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra were obtained with a Perkin–Elmer 283 spectrometer from samples prepared as mulls in Nujol or Fluorolube and pressed between KBr, CsBr, or CsI windows. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on either a JEOL FX 90Q or a JNM-FX 270 FT-NMR spectrometer. ^{31}P positive chemical shifts are downfield from 85% H_3PO_4.

*Synthesis of the diastereomers $IrClH(P(t\text{-}Bu)_2CH_2CHCH_2CH)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ (**1a** and **1b**)*

$P(t\text{-}Bu)_2CH_2CHCH_2CH_2$ (0.894 g) was combined with $[IrCl(C_8H_{14})_2]_2$ (1.000 g) in diethyl ether or toluene at 25 °C. Removal of solvent and cyclooctene at reduced pressure provided a mixture of two products.

Complexes **1a** + **1b**: IR (Nujol mull) ν(Ir–H) 2300; ν(Ir–Cl) 245 cm^{-1}; ^1H NMR (C_7D_8, 270 MHz) δ, -44.8 (t, $^2J(H\text{-}P_{cis})$ 13.2 Hz, Ir–H, **1a**), -42.0 ppm (t, $^2J(H\text{-}P_{cis})$ 12.6 Hz, Ir–H, **1b**), complex cyclopropyl and t-butyl regions; ^{31}P NMR (C_7D_8, 109.16 MHz) δ 94.4, 38.2 (dd, $^2J(P\text{-}P_{trans})$ 366.3 Hz, **1a**), 88.5, 38.3 ppm (dd, $^2J(P\text{-}P_{trans})$ 360.5 Hz, **1b**); Anal. Found: C, 45.72; H, 7.90. $C_{24}H_{50}ClIrP_2$ calcd.: C, 45.88; H, 8.02%.

If the reaction is carried out in diethyl ether below -10 °C, product **1a** is formed selectively in approximately a 5/1 ratio. When the temperature is raised to 25 °C, the yield of product **1a** decreases and the yield of product **1b** increases, as deduced from the relative peak heights in the ^{31}P NMR spectrum or from the relative heights of the hydride resonances in the ^{1}H NMR spectrum. After ~72 h at room temperature an equilibrium mixture of the two diastereomers is formed with a product ratio of **1a**/**1b** of 1/3. Below 20 °C the isomerization does not occur at observable rates.

Synthesis of $IrClH_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ *(2) and* $IrClD_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ *(2a)*

Dihydrogen was bubbled through a mixture of **1a** + **1b** in toluene. Removal of solvent gave **2** quantitatively. Substitution of dideuterium for dihydrogen in this experiment resulted in **2a**, in which deuterium substitution occurs at the metal center. The spectral data for **2a** are identical with those for **2** except for the appearance of Ir–D bands in the IR spectrum in place of the hydride bands of **2**, and the disappearance of the hydride resonance at δ −32.19 ppm.

Complexes **2** + **2a**: IR (Nujol mull) ν(Ir–H) 2245, 2295 cm^{-1} (ν(Ir–D) 1612, 1653 cm^{-1}), ^{1}H NMR (C_7D_8, 270 MHz) δ −32.19 (t, $^2J(H\text{-}P_{cis})$ 13.0 Hz), 0.35 (m, cyclopropyl), 0.51 (m, cyclopropyl), 1.32 (t, ^3J(H–P) 6.2 Hz, CH_3), 2.09 ppm (m, CH_2); ^{13}C NMR (C_7D_8, 67.8 MHz) δ 8.63 + 9.66 (s, cyclopropyl), 27.92 (d of d, ^1J(P–C) 20.5, ^3J(P–C) 8.8 Hz), 30.69 (s, CCH_3), 35.88 ppm (d of d, ^1J(P–C) 20.5, ^3J(P–C) 8.8 Hz, CCH$_3$); ^{31}P NMR (C_7D_8, 109.16 MHz) δ 55.80 (s) ppm. Anal. Found: C, 45.86; H, 7.85. $C_{24}H_{52}ClIrP_2$ calcd.: C, 45.75, H, 8.31%.

Synthesis of $\overline{IrClH(P(t\text{-}Bu)_2CH_2C(CH_3)CH})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$ *(3)*

A mixture of **1a** + **1b** was placed in chloroform. Isomerization to **3** was complete in approximately 72 h. Isomerization in toluene takes much longer. IR (Nujol mull) 1928, ν(Ir–H) 2305, ν(Ir–Cl) 255 cm^{-1}; ^{1}H NMR (C_7D_8, 270 MHz), δ −40.7 (^2J(P–H) 13.9 Hz), 0.28, 0.49 + 0.84 (m, cyclopropyl), 1.29 (d, ^3J(H–P) 11.7 Hz, CCH_3), 1.31 (d, ^3J(H–P) 12.7 Hz, CCH_3), 1.37 (d, ^3J(H–P) 12.2 Hz, CCH_3), 1.48 (d, ^3J(H–P) 12.5 Hz, CCH_3), 1.93 (s), 2.11 (m), 2.22 (d, J(H–P) 7.3 Hz), 6.47 ppm (d, J(H–P) 7.3 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ 7.06 + 7.96 (s, cyclopropyl), 22.53 (d, J 22.0 Hz), 23.80 (d, J 14.7 Hz), 29.53 + 30.28 + 30.64 + 31.29 (s, CCH_3), 32.01 (d, J 29.3 Hz), 34.57 (d, J 19.5 Hz), 36.45 (d, J 17.1 Hz), 37.55 (d, J 14.7 Hz), 119.61(s), 143.91 ppm (d, J 14.6 Hz). Anal. Found: C, 45.70; H, 7.88. $C_{24}H_{50}ClIrP_2$ calcd.: C, 45.88; H, 8.02%.

Synthesis of $\overline{IrClH(CO)(P(t\text{-}Bu)_2CH_2C(CH_3)CH})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$ *(4)*

Carbon monoxide was bubbled through a solution of **3** in methylene chloride. Removal of solvent afforded quantitative isolation of **4**. IR (Nujol mull) 1930, ν(Ir–H) 2165, ν(CO) 1985, ν(C=C) 1600(broad), ν(Ir–Cl) 225 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ −7.77 (d of d, ^2J(P–H) 14.3, ^2J(P–H) 18.0 Hz), 0.26, 3.9, 0.51 (m, cyclopropyl), 0.57 (d, J 7.9 Hz), 1.32–1.53 (m, t-butyl region), 1.89(s), 2.07(m), 6.32 (d, J 5.5 Hz); ^{13}C NMR ($CDCl_3$, 67.8 MHz) alkyl and cyclopropyl resonances and 112.27(s), 136.84 (d, J 12.2 Hz), 182.82(s) ppm; ^{31}P NMR ($CDCl_3$, 109.16 MHz) 59.32, 30.20 ppm (^2J(P–P) 307.2 Hz).

Synthesis of $IrClH_2(P(t\text{-}Bu)_2CH_2CH(CH_3)_2)(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})$ *(5)*

Dihydrogen was bubbled through a solution of **3** in $CHCl_3$ to afford **5** in quantitative yield after removal of the solvent. ^{1}H NMR ($CDCl_3$, 270 MHz) −33.11 (t, $^2J(H\text{-}P_{cis})$ 14.6 Hz), δ 0.32(m) + 0.56(m) (cyclopropyl), 1.03 (d, J 8.0 Hz) (isobutylmethyl groups), 1.30, 1.31, 1.34, 1.35, 1.93(m), 2.11(m) ppm; ^{31}P NMR ($CDCl_3$, 109.16 MHz) δ 56.25, 52.04 ppm (J(P–P) 334.0 Hz).

X-ray study of $IrClH(CO)(P(t\text{-}Bu)_2CH_2C(CH_3)CH)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ (**4**)

Single crystals suitable for X-ray diffraction were obtained through recrystallization of the compound from pentane. Preliminary Weissenberg photography showed the crystals to be monoclinic. Systematic absences were consistent with the space group C_{2h}^5-$P2_1/n$.

Table 1 summarizes the crystal data and intensity collection (T −151°C). A Picker FACS-1 diffractometer was used to obtain cell constants and collect intensity data in a manner previously described [7]. Checks every 100 reflections during data collection on the intensities of six standard reflections revealed an average decomposition of 28% among these representative reflections.

Standard Patterson and Fourier techniques were used to solve the structure. The positions of the Ir, Cl, and two P atoms were found initially. The positions of

TABLE 1

CRYSTALLOGRAPHIC DETAILS FOR $IrClH(CO)(P(t\text{-}Bu)_2CH_2C(CH_3)CH)(P(t\text{-}Bu)_2CH_2\text{-}CHCH_2CH_2)$

Formula	$C_{25}H_{50}ClIrOP_2$
Formula weight	657 30
Space group	C_{2h}^5-$P2_1/n$
a (Å)	15.610(14)
b (Å)	15.763(16)
c (Å	11.973(13)
β (°)	104.74(5)
V (Å^3)	2848
Z	4
ρ_c (g cm^{-3}) (−151°C)	1.533
Crystal dimensions (mm)	0.185×0.164×0 972
μ(Cu-K_α) (cm^{-1})	86.1
Temperature (°C)	−151 [a]
Transmission factors	0.133–0.316
Scan mode	θ–2θ
Scan speed	2° in 2θ min^{-1}
Scan range (°)	1.99 below K_{α_1} to 1.99 above K_{α_2}
Background counts (s)	10 at each end of scan with rescan option [b]
Data collected	$\pm h$, $+k$, $+l$
2θ limits (°)	5.0–115.0
Unique data	3423
Unique data with $F_o^2 > 3\sigma(F_o^2)$	2326
Final no. of variables	271
$R(F)$	0.089
$R_w(F)$	0.095
$R(F^2)$	0.148
$R_w(F^2)$	0.196
Error in observation of unit weight, e^2	2.02

---

[a] The low-temperature system is based on a design by J.C. Huffman, Ph.D. Thesis, Indiana University, 1974. [b] The diffractometer was run under the Vanderbilt disk orientated system (P.G. Lenhert, J Appl. Crystallogr., 8 (1975) 568.

TABLE 2

POSITIONAL PARAMETERS AND ESTIMATED STANDARD DEVIATIONS FOR $\mathrm{IrClH(CO)(P(t\text{-}Bu)_2CH_2C(CH_3)CH)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)}$

Atom	*x*	*y*	*z*
Ir	0.241912(57)	0.154451(46)	0.042653(65)
P(1)	0.23936(33)	0.08942(31)	0.21756(38)
P(2)	0.26351(33)	0.19191(29)	−0.14078(39)
Cl	0.31277(36)	0.28592(33)	0.13639(44)
O	0.0515(13)	0.2308(11)	−0.0068(19)
C(1)	0.1557(18)	0.0045(16)	0.1691(21)
C(2)	0.1561(12)	−0.0148(12)	0.0448(17)
C(3)	0.1895(13)	0.0425(13)	−0.0154(17)
C(4)	0.1070(16)	−0.0972(14)	−0.0016(22)
C(5)	0.1954(19)	0.1504(16)	0.3231(19)
C(6)	0.2708(31)	0.2064(27)	0.4016(29)
C(7)	0.1225(23)	0.2066(22)	0.2596(27)
C(8)	0.1668(31)	0.0862(25)	0.4082(30)
C(9)	0.3436(18)	0.0329(21)	0.2893(26)
C(10)	0.4234(16)	0.0927(33)	0.3010(33)
C(11)	0.3553(21)	−0.0330(22)	0.1996(41)
C(12)	0.3469(19)	−0.0055(23)	0.3986(29)
C(13)	0.1925(12)	0.1362(11)	−0.2583(16)
C(14)	0.0885(16)	0.1552(14)	−0.2950(23)
C(15)	0.0276(14)	0.0877(18)	−0.3605(21)
C(16)	0.0258(17)	0.1102(22)	−0.2439(25)
C(17)	0.2452(13)	0.3082(11)	−0.1888(16)
C(18)	0.3256(16)	0.3638(13)	−0.1325(20)
C(19)	0.2266(17)	0.3190(13)	−0.3172(21)
C(20)	0.1655(15)	0.3433(13)	−0.1486(20)
C(21)	0.3742(13)	0.1570(12)	−0.1558(18)
C(22)	0.4480(11)	0.1876(17)	−0.0523(19)
C(23)	0.3974(16)	0.1815(17)	−0.2676(21)
C(24)	0.3785(15)	0.0563(13)	−0.1467(22)
C(25)	0.1253(16)	0.2008(14)	0.0175(25)

the remaining non-hydrogen atoms were obtained from a series of electron density syntheses after absorption and decomposition corrections had been applied.

Approximate positions of the hydrogen atoms of the methyl groups were found in electron density maps. These positions were subsequently idealized as were the positions of the remaining hydrogen atoms (C–H 0.95 Å, $B(\mathrm{H}) = B(\mathrm{C}) + 1.0$ Å^2). These hydrogen atom positions were not varied in the refinement. No evidence for the position of the hydride ligand could be obtained.

The final least-squares refinement was carried out on F_o^2 with all unique data, including those with $F_o^2 < 0$. Agreement indices are in Table 1. Table 2 presents the final positional parameters, Table 3 * the thermal parameters, Table 4 * the hydrogen atom positions, and Table 5 * a listing of $10|F_o|$ vs. $10|F_c|$.

---

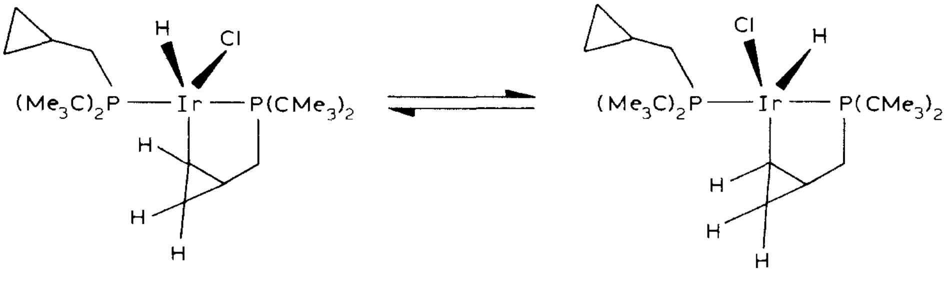
* See NAPS document no. 04214 for 18 pages of supplementary material. Order from NAPS % Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance in U.S. funds only \$7.75 for photocopies or \$4.00 for microfiche. Outside the U.S. and Canada, add postage of \$4.50 for the first 20 pages and \$1.00 for each 10 pages of material thereafter. \$1.50 fir microfiche postage.

Results

When $\mathrm{P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2}}$ is combined with $\mathrm{[IrCl(C_8H_{14})_2]_2}$ in diethyl ether or toluene at 25 °C a mixture of two products (**1a** and **1b** in approximately equal amounts) is obtained. The ^{31}P NMR spectrum clearly shows the presence of two species each having two inequivalent phosphorus atoms. The two phosphorus resonances of compound **1a** are at δ 38.2 and 94.4 ppm with a coupling constant of $^{2}J(\mathrm{P-P})$ 366.3 Hz. Similarly, the phosphorus resonances of **1b** occur at δ 88.5 and 38.3 ppm ($^{2}J(\mathrm{P-P})$ 360.5 Hz). The downfield chemical shifts to δ 94.4 and 88.5 ppm indicate that the phosphorus atoms that give rise to these resonances are part of a five-membered ring. (A discussion of the effect of ring size on ^{31}P chemical shifts has appeared previously [8].) In the ^{1}H NMR spectra resonances at δ -44.8 (t, $^{2}J(\mathrm{H-P}_{cis})$ 13.2 Hz) and -42.0 ppm (t, $^{2}J(\mathrm{H-P}_{cis})$ 12.6 Hz) are assigned to hydride ligands on **1a** and **1b**, respectively. Such high field shifts have been previously observed for hydride ligands on neutral, 5-coordinate, 16-electron $\mathrm{Ir^{III}}$ complexes [9]. In the IR spectrum bands for these hydrides are observed at 2300 cm^{-1}. The cyclopropyl and t-butyl regions of the ^{1}H NMR spectra are complex. The peak farthest downfield is at δ 2.09 ppm. The ^{13}C NMR spectrum shows no resonances further downfield than 36 ppm. Unusual peaks in the ^{13}C NMR spectrum are observed at δ -7.97 and -9.24 ppm. The Ir–Cl stretch is observed at 255 cm^{-1} in the IR spectrum.

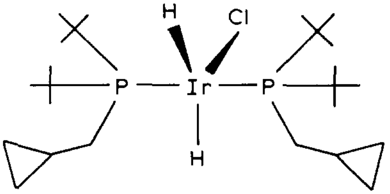
From the ^{31}P NMR spectra we conclude that both **1a** + **1b** have a phosphorus atom that is part of a five-membered ring. Furthermore, since the largest possible ring formed by cyclometallation of a t-butyl group (without alkyl migration) would be a four-membered ring, activation of the cyclopropane must have occurred. Carbon–carbon bond activation of the cyclopropane would not give a hydride except by further isomerization to a ring-opened product, similar to that obtained with Pt $\mathrm{[\overline{PtCl(P(t\text{-}Bu)_2CHC(CH_3)CH_2})(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})]}$ [5b]. Assignment of ring-opened structures for **1a** + **1b** is not consistent with the spectral data and reaction chemistry (vide infra). Carbon–hydrogen bond activation of the cyclopropane ring would give a hydride and a five-membered metallacycle.

The above data are consistent with **1a** and **1b** being diastereomers. Each is a 5-coordinate, 16-electron $\mathrm{Ir^{III}}$ complex containing a σ-bound cyclopropane.



(1a) **(1b)**

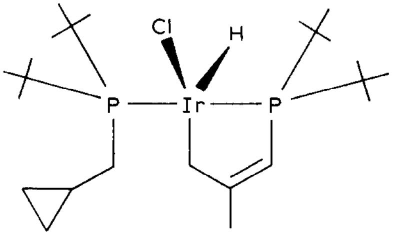
When $\mathrm{H_2}$ is bubbled through a mixture of **1a** + **1b** in toluene a single product, **2**, is formed within minutes. The ^{1}H NMR spectrum of **2** shows a triplet at δ -32.19 ppm ($^{2}J(\mathrm{H-P}_{cis})$ 13.0 Hz), resulting from hydrides coupled to two equivalent phosphines, multiplets at δ 0.35 and 0.51 ppm, which are typical of *cis* and *trans* protons on a cyclopropyl ring, a triplet at δ 1.32 ppm (^3J(H–P) 6.2 Hz) resulting from virtual coupling of the equivalent phosphines to the t-butyl groups, and a multiplet at δ 2.09 ppm resulting from CH_2 groups coupled to phosphorus and the methine cyclopropyl hydrogen nuclei. The ^{31}P NMR spectrum shows a singlet at δ 55.80 ppm that becomes a triplet when the hydride nuclei are allowed to couple while all other protons remain decoupled. The $^{13}C\{^1H\}$ NMR spectrum shows singlets in the cyclopropyl region at δ 8.63 and 9.66, a doublet of doublets at 27.92 ppm (^1J(P–C) 20.5, ^3J(P–C) 8.8 Hz) resulting from the CH_2 groups, a singlet at δ 30.69 from the methyl groups of the t-butyl groups, and a doublet of doublets at δ 35.88 ppm (^1J(P–C) 20.5, ^3J(P–C) 8.8 Hz) from the quaternary carbon atom. In the IR spectrum the two hydride bands are observed at ν(Ir–H) 2245, 2295 cm^{-1} with the analogous deuteride bands at ν(Ir–D) 1612, 1653 cm^{-1} giving ν(Ir–H)/ν(Ir–D) ratios of 1.393 and 1.388, respectively. The above data lead to the unambiguous characterization of **2** as *trans*-$IrClH_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$. The spectral data



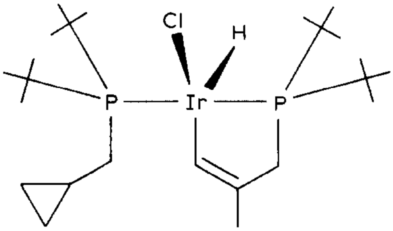
(2)

on the phosphine part of this molecule are very similar to those that we previously reported for *trans*-$PtCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ [5b]. The formation of *trans*-$IrClH_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$ (**2**) when H_2 is bubbled through **1a** + **1b** is further evidence that no skeletal rearrangement of the metallated cyclopropyl phosphine has occurred in the formation of **1a** + **1b**.

When a mixture of **1a** + **1b** is placed in methylene chloride, chloroform, or other polar solvents formation of product **3** is observed. This complex also has a metal hydride resonance shifted to high field that occurs as a distorted triplet at δ −40.7 (^2J(P–H) 13.9 Hz) in the ^1H NMR spectrum. There is a band at 2305 cm^{-1} in the IR spectrum. The cyclopropyl region of this compound is less complex than that of **1a** + **1b**. Selective decoupling experiments ($CDCl_3$) show that the peak at δ 0.2464 is coupled to the peak at 0.5437 ($J \sim 8$ Hz) and to the peak at 0.8439 ppm ($J \sim 8$ Hz); these in turn are also coupled to each other ($J \sim 3$ Hz). Four sets of doublets are observed in the t-butyl region, indicative of four types of inequivalent t-butyl protons. The multiplet at δ 2.11 ppm is assigned to a methylene group connecting a phosphorus atom with a cyclopropane ring. The singlet at δ 1.93 is consistent with a methyl group, the doublet at 2.22 ppm (J(H–P) 7.3 Hz) may be assigned to allylic protons coupled to a phosphorus atom, and the doublet at δ 6.47 ppm (J(H–P) 7.3 Hz) to a vinylic proton coupled to a phosphorus atom. The ^{13}C NMR spectrum clearly shows cyclopropyl and t-butyl carbon atoms between δ 0 and 35 ppm and alkene carbon atoms at δ 119.61(s) and 143.91 ppm (d, J 14.6 Hz). The fully proton coupled ^{13}C NMR spectrum indicates that the peak at δ 119.61 (J(C–H) 144.04 Hz) is from a methine carbon atom, while the peak at 143.91 ppm is from an alkene carbon atom with no protons on it. In the δ 15–35 ppm range the fully proton coupled ^{13}C NMR spectrum is complicated by severe overlap of the ^{13}C multiplets. Assignments in this area were made with the use of the INEPT pulse sequence [10]. The peaks at δ 22.53 and 32.01 ppm are methylene resonances, while the peak at δ 23.80 ppm is a methyl resonance. The t-butyl and cyclopropyl carbon atoms have also been identified. The ^{31}P NMR spectrum shows that two inequivalent *trans* phosphine groups are present δ 66.7, 38.7 ppm ($^{2}J(\text{P–P}_{trans})$ 351.7 Hz). The above data indicate that **3** has a carbon ring skeleton similar to the previously characterized σ-allyl platinum complex, $PtCl(P(t\text{-}Bu)_2CHC(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ [5b]. However the IR spectrum for **3** shows a band at 1928 cm^{-1} that appears to be inconsistent with possible structures **3a** or **3b**.

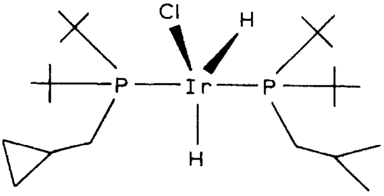


(3a)



(3b)

But two further lines of evidence support either of these structures. When CO is bubbled through a solution of **3** in $CDCl_3$ compound **4** is isolated. The ^{31}P, ^{1}H, and ^{13}C NMR spectra of **4** indicate that it is the simple CO adduct of **3**. Also, the IR spectrum exhibits a shift of 140 cm^{-1} in the ν(Ir–H) band to 2165 and a ν(CO) band at 1985 cm^{-1}. A broad weak band at 1600 cm^{-1} is now observed. It is possible that this band is also present in **3** but cannot be distinguished from the base line. A band occurs at 1930 cm^{-1} that is analogous to that at 1928 cm^{-1} in **3**. Both this band and the band at 2165 cm^{-1} are enhanced by the presence of the CO ligand. Also consistent with **3a** and **3b** is the formation of **5** when H_2 is bubbled through a solution of **3** in $CHCl_3$.



(5)

No suitable crystals of **3** could be obtained. However, crystals of **4** were obtained and an X-ray crystal structure was carried out to establish the nature of the ring system in **4** and **3**. These results clearly establish that system to be the one shown for **3b** above. The nature of the IR bands at 1930 in **4** and 1928 cm^{-1} in **3** remains unexplained.

As illustrated in Fig. 1, the Ir atom of **4** is in a distorted octahedral array of donor ligands with the hydride ligand at the vacant coordination site. Bond distances and angles are given in Table 6. Figure 2 is a stereodrawing of the molecule. The crystal structure consists of neutral monomers with the shortest intermolecular non-hydrogen separation (3.27(3) Å) occurring between atoms O and C(4) of neighboring molecules.

The portion of the molecule defined by the Ir, Cl, P(1), P(2), and C(3) atoms is very similar to the square planar complex $PtCl(P(t\text{-}Bu)_2CHC(CH_3)CH_2)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ [5b] except for the position of the double bond in the five-membered ring. In both complexes the chelating phosphine ligand causes significant deviation from idealized coordination geometry about the metal atom. Relevant angles for Ir are C(3)–Ir–P(1) 79.9(5), C(3)–Ir–P(2) 92.3(5), C(25)–Ir–P(1) 94.3(8), C(25)–Ir–P(2) 96.5(8), C(25)–Ir–C(3) 89.6(9), P(1)–Ir–Cl = 93.9(2),

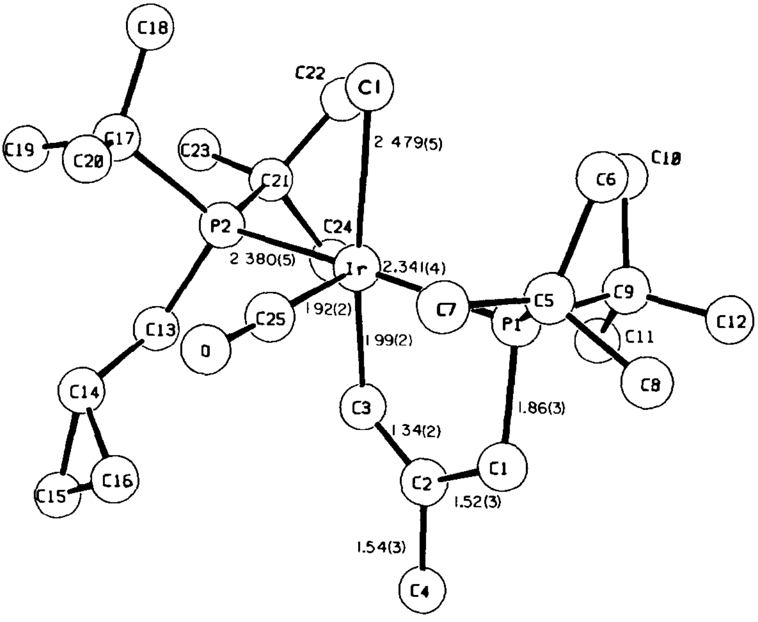


Fig. 1. Drawing of the $IrClH(CO)(P(t\text{-}Bu)_2CH_2C(CH_3)CH)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ molecule. The atoms have been drawn as spheres with arbitrary radii. Selected bond distances (Å) have been included in the figure.

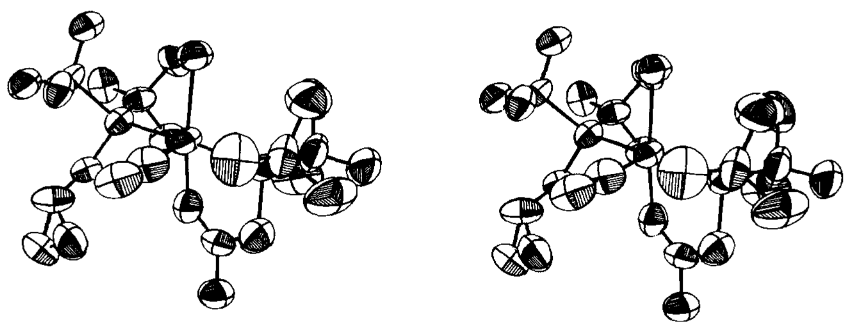


Fig. 2. Stereoscopic view of the $IrClH(CO)P(t\text{-}Bu)_2CH_2C(CH_3)CH)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)$ molecule. Thermal ellipsoids have been drawn at the 50% probability level.

TABLE 6

BOND DISTANCES (Å) AND BOND ANGLES (°) IN $\mathrm{IrClH(CO)(P(t\text{-}Bu)_2CH_2C(CH_3)CH)(P(t\text{-}Bu)_2CH_2CHCH_2CH_2)}$

Ir–Cl	2.479(5)	C(5)–C(6)	1.576(48)
Ir–P(1)	2.341(4)	C(5)–C(7)	1.489(44)
Ir–P(2)	2.380(5)	C(5)–C(8)	1.579(36)
Ir–C(3)	1.994(21)	C(9)–C(10)	1.540(43)
Ir–C(25)	1.912(23)	C(9)–C(11)	1.539(49)
P(1)–C(1)	1.857(26)	C(9)–C(12)	1.430(36)
P(1)–C(5)	1.853(24)	C(17)–C(18)	1.538(32)
P(1)–C(9)	1.862(27)	C(17)–C(19)	1.499(31)
P(2)–C(13)	1.785(20)	C(17)–C(20)	1.546(24)
P(2)–C(17)	1.921(17)	C(21)–C(22)	1.539(32)
P(2)–C(21)	1.865(18)	C(21)–C(23)	1.524(28)
C(1)–C(2)	1.520(30)	C(21)–C(24)	1.591(28)
C(2)–C(3)	1.341(25)	C(25)–O	1.210(28)
C(2)–C(4)	1.539(29)		
C(13)–C(14)	1.598(33)		
C(14)–C(15)	1.508(34)		
C(14)–C(16)	1.463(30)		
C(15)–C(16)	1.447(36)		
Cl–Ir–P(1)	93.92(18)	C(3)–C(2)–C(4)	126.9(19)
Cl–Ir–P(2)	93.36(17)	Ir–C(3)–C(2)	126.1(14)
Cl–Ir–C(3)	173.57(58)	P(2)–C(13)–C(14)	120.5(12)
Cl–Ir–C(25)	92.79(73)	C(13)–C(14)–C(15)	118.2(18)
P(1)–Ir–P(2)	166.64(17)	C(13)–C(14)–C(16)	122.3(22)
P(1)–Ir–C(3)	79.95(55)	C(15)–C(14)–C(16)	58.3(16)
P(1)–Ir–C(25)	94.33(81)	C(14)–C(15)–C(16)	59.3(17)
P(2)–Ir–C(3)	92.28(53)	C(14)–C(16)–C(15)	62.4(17)
P(2)–Ir–C(25)	96.49(82)	P(1)–C(5)–C(6)	110.3(23)
Ir–P(1)–C(1)	101.95(77)	P(1)–C(5)–C(7)	109.2(16)
Ir–P(1)–C(5)	118.46(72)	P(1)–C(5)–C(8)	108.8(21)
Ir–P(1)–C(9)	114.22(77)	C(6)–C(5)–C(7)	109.2(28)
C(1)–P(1)–C(5)	103.5(11)	C(6)–C(5)–C(8)	105.4(23)
C(1)–P(1)–C(9)	105.2(14)	C(7)–C(5)–C(8)	113.9(27)
Ir–P(2)–C(13)	113.55(54)	P(1)–C(9)–C(10)	109.9(22)
Ir–P(2)–C(17)	117.91(52)	P(1)–C(9)–C(11)	104.2(23)
Ir–P(2)–C(21)	111.60(67)	P(1)–C(9)–C(12)	116.6(21)
C(5)–P(1)–C(9)	111.4(14)	C(10)–C(9)–C(11)	103.8(27)
C(13)–P(2)–C(17)	102.6(9)	C(10)–C(9)–C(12)	109.6(28)
C(13)–P(2)–C(21)	100.6(8)	C(11)–C(9)–C(12)	111.8(31)
C(17)–P(2)–C(21)	108.9(8)	P(2)–C(17)–C(18)	111.7(15)
P(1)–C(1)–C(2)	105.8(14)	P(2)–C(17)–C(19)	113.0(14)
C(1)–C(2)–C(3)	119.4(18)	P(2)–C(17)–C(20)	108.5(11)
C(1)–C(2)–C(4)	113.3(18)	C(18)–C(17)–C(19)	108.0(15)
C(18)–C(17)–C(20)	106.9(16)		
C(19)–C(17)–C(20)	108.5(18)		
P(2)–C(21)–C(22)	110.6(13)		
P(2)–C(21)–C(23)	116.3(16)		
P(2)–C(21)–C(24)	108.2(12)		
C(22)–C(21)–C(23)	109.3(15)		
C(22)–C(21)–C(24)	104.4(19)		
C(23)–C(21)–C(24)	107.3(16)		

P(2)–Ir–Cl 93.3(2)°. The angles C(3)–Ir–Cl (173.6(6)°) and P(1)–Ir–P(2) (166.6(2)°) are indicative of the expected folding of the molecule toward the smaller hydride ligand *trans* to atom C(25). These distortions may be aggravated by close contact between the Cl atoms and CH_3 groups (Cl ··· C(18) 3.50(2) and Cl ··· C(6) 3.63(3) Å). Short intramolecular distances (3.672(3) and 3.681(3) Å) between Cl and CH_3 appear to be the major cause of deviation from square-planar geometry in the closely related complex $(\overline{\text{PdClP(t-Bu)}_2\text{CHC(CH}_3\text{)CH}_2})_2$ [5a].

The planes of the octahedral array and the chelate ring of the Ir complex are slightly distorted, with some of the deviations from the least-squares planes exceeding 0.1 Å. In contrast, planar coordination geometry is preserved for the Pt and Pd σ-allyl complexes. A possible explanation may be found in the hybridizations of carbon atoms C(3) and C(1), which are reversed in the Ir complex relative to the Pd and Pt complexes. The P(1)–C(1)–C(2) angles for Ir, Pd, and Pt complexes are 105.8(14), 114.0(3), and 111.3(6)°, respectively. The smaller angle in the Ir metallacycle, which results from sp^3 hybridization of atom C(1), is compensated for by a larger Ir–C(3)–C(2) angle: 126.1(14) vs. 119.1(2)° for Pd–C(3)–C(2) and 121.1(5)° for Pt–C(3)–C(2). Thus the five-membered ring in the Ir σ-vinyl complex is skewed relative to the rings in the Pd and Pt σ-allyl complexes.

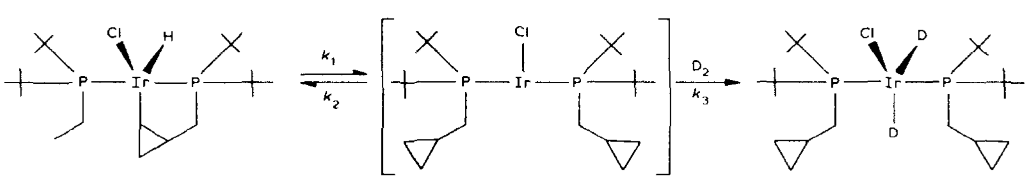
Bond distances within the Ir coordination sphere and the metallacycle are given in Fig. 1. Those of the metallacycle are comparable with bond distances in the chelate ring of $(\overline{\text{PdClP(t-Bu)}_2\text{CHC(CH}_3\text{)CH}_2})_2$ [5a] and are in the expected range.

The Ir–Cl bond distance, 2.479(5) Å, is typical of octahedral Ir^{III} complexes in which Cl is *trans* to an sp^2 hybridized carbon atom. Examples are $IrCl_2(p\text{-}MeOC_6H_3NNH)(PPh_3)_2$, Ir–Cl 2.493(2) [11], and $IrCl(CO)(PPh_3)_2(B_{10}C_{14}H_{11})(B_{10}C_{14}H_{13})$, Ir–Cl 2.512(5) Å [12]. The Ir–C distances for these two complexes (2.011(8), 2.08(2) Å) [11,12] are also comparable with the Ir–C(3) distance (1.99(2) Å) observed in the present complex. The Ir^{III}–P distances (Ir–P(1) 2.341(4) and Ir–P(2) 2.380(5) Å) are normal. For instance, the average Ir–P bond length in both bis(triphenylphosphine) complexes previously cited is 2.379(6) Å [11,12]. The two Ir–P bond lengths in the present compound may differ because of the chelating nature of the phosphine ligand on atom P(1). In $IrH_2Cl(Ph_2P(CH_2)_2CHCH(CH_2)_2PPh_2)$ both *trans* phosphines are contained in chelate rings as part of the μ^3-diphosphine ligand and both Ir–P bonds are foreshortened (2.301 and 2.283(4) Å) [13]. The Ir–C(25) bond distance (1.91(2) Å) is the same as that in $IrH(Me_2SiOSiMe_2)(CO)(PPh_3)_2$ (1.903(8) Å), in which the CO ligand is also *trans* to a hydride ligand [14].

Possible reaction pathways

The formation of **1a** vs. **1b** presumably is a function of the direction of approach of the cyclopropyl C–H bond to the metal center. We have no evidence as to which structure applies to **1a**, the diastereomer formed selectively at −20 °C. At 25 °C isomerization is complete in 72 h with **1a**/**1b** = 1/3. That this isomerization reaction is very slow may be the result of required bond rotations.

A low probability for the bond rotations required for the isomerization could explain why the rate of isomerization (k_2) is slow relative to the rate of hydrogenation (k_3). Reaction of **1a** and **1b** with D_2 occurs in minutes, producing only **2a**. No D is incorporated in the cyclopropyl ring and no H is left on the Ir center. Alternatively, this product may result from reductive elimination of the cyclopro-

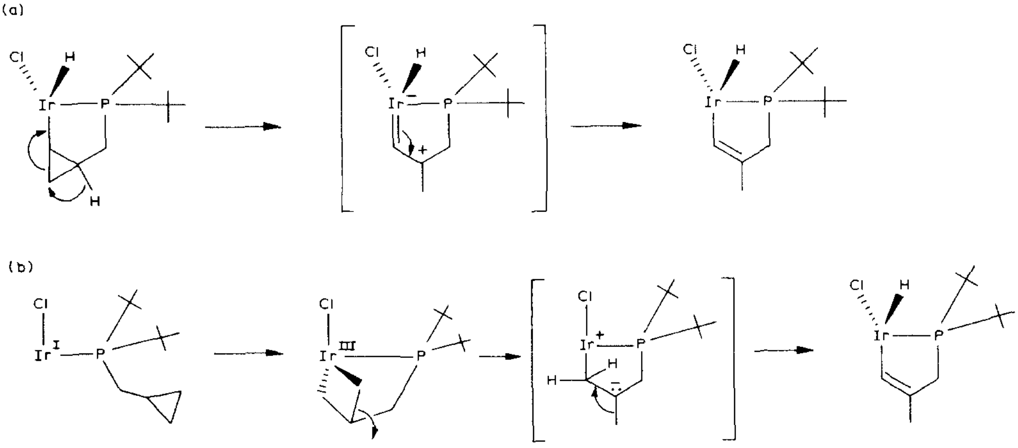


(1a,b)

(2a)

pane induced by approach of D_2 to the metal center with concurrent formation of Ir–D bonds. In this case a pseudo-rotation mechanism could be involved for the isomerization. We have no data that permit us to choose between these pathways.

The isomerization of **1a** + **1b** to **3** shows that a neutral, 5-coordinate, 16-electron Ir^{III} complex containing a chelating σ-bound cyclopropane can undergo a ring opening to form a chelating σ-vinyl complex. Whether this isomerization proceeds by (a) direct ring opening of the σ-bound cyclopropane or by (b) reductive elimination of the cyclopropane followed by C–C bond activation in the polar solvent is not known. Either scheme could produce the observed products.



SCHEME 1

Scheme 1(b) is complementary to the reversible metallation proposed for addition of D_2 to the Ir center. Further isomerization may have occurred under the harsher reaction conditions used in the formation of the σ-allyl complexes of Pt and Pd [5] (120 °C in 2-MeOEtOH). Under such harsh conditions the propene fragment of a postulated σ-vinyl complex could reductively eliminate and rearrange to form the more stable alkene. The rearranged propene fragment could then oxidatively add to Pt or Pd to form the σ-allyl complex.

Acknowledgments

This research was kindly supported by the National Science Foundation (CHE83-08076). We thank Johnson-Matthey, Inc., Malvern, Pennsylvania for the loan of Ir salts used in this study.

References

1 G.W. Parshall, Catalysis, 1 (1977) 335.

2 (a) B.L. Shaw, J. Organomet. Chem., 200 (1980) 307 and refs. therein; (b) R.G. Goel and W.O. Ogini, Organometallics, 1 (1982) 654 and refs. therein.

3 (a) A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 104 (1982) 352; (b) A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 105 (1983) 3929; (c) R.H. Crabtree, M.F. Mellea, J.M. Mihelcic, and J.M. Quirk, J. Am. Chem. Soc., 104 (1982) 107; (d) R.H. Crabtree, J.M. Milhelcic, and J.M. Quirk, ibid., 101 (1979) 7738.

4 (a) S. Sarel, Acc. Chem. Res., 11 (1978) 204; (b) J. Rajaram and J.A. Ibers, J. Am. Chem. Soc., 100 (1978) 829; (c) T.H. Tulip and J.A. Ibers, J. Am. Chem. Soc., 100 (1978) 3252; (d) ibid., 101 (1979) 4201; (e) K.C. Bishop, Chem. Rev., 76 (1976) 461.

5 (a) W.J. Youngs, J. Mahood, B.L. Simms, P.N. Swepston, J.A. Ibers, M. Shang, J. Huang, and J. Lu, Organometallics, 2 (1983) 917; (b) W.J. Youngs and J.A. Ibers, Organometallics, 2 (1983) 979.

6 W.J. Youngs and J.A. Ibers, J. Am. Chem. Soc., 105 (1983) 639.

7 J.M. Waters and J.A. Ibers, Inorg. Chem., 16 (1977) 3273.

8 P.E. Garrou, Chem. Rev., 81 (1981) 229.

9 L. Masters, B.L. Shaw, and R.E. Stainbank, J. Chem. Soc., Dalton Trans., (1972) 664.

10 (a) G.A. Morris and R. Freeman, J. Am. Chem. Soc., 101 (1979) 760; (b) D.M. Doddrell and D.T. Pegg, J. Am. Chem. Soc., 102 (1980) 6388.

11 P.L. Bellon, G. Caglio, M. Manassero, and M. Sansoni, J. Chem. Soc., Dalton Trans., (1974) 897.

12 K.P. Callahan, C.E. Strouse, S.W. Layten, and M.F. Hawthorne, J. Chem. Soc., Chem. Commun., (1973) 465.

13 G.R. Clark, M.A. Mazid, D.R. Russell, P.W. Clark, and A.J. Jones, J. Organomet. Chem., 166 (1979) 109.

14 M.D. Curtis, J. Greene, and W.M. Butler, J. Organomet. Chem., 164 (1979) 371.