1562 *Organometallics* **1982**, *1*, 1562-1567

Allyliridium Phosphite Complexes.[1] Synthesis and Chemistry†

E. L. Muetterties,* K. D. Tau, J. F. Kirner, T. V. Harris, and J. Stark

Department of Chemistry, University of California, Berkeley, California 94720

M. R. Thompson and V. W. Day*

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, and The Crystalytics Company, Lincoln, Nebraska 68510

Received June 14, 1982

Reaction of allyllithium and chloroiridium 1,5-cyclooctadiene dimer yielded allyliridium 1,5-cyclooctadiene, a thermally reactive molecule. Direct reactions of the allyliridium complex with 1, 2, and 3 equiv of trimethyl phosphite yielded, respectively, $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]$, $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]_2$, and $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$ (1,5-COD = 1,5-cyclooctadiene). The first and last allyliridium complexes have NMR spectral features consistent with five-coordinate square-pyramidal structures with the axial site occupied by a trimethyl phosphite ligand, whereas those of the second complex are better accounted for in a trigonal-bipyramidal form with equatorial phosphite ligands. Hydrogen reacted with the last two complexes to give mixtures of $HIr[P(OCH_3)_3]_4$ and the facial and meridianal isomers of $H_3Ir[P(OCH_3)_3]_3$; small amounts of another hydride complex were generated from the bis(phosphite) complex. None of the allyliridium complexes nor any of their products in the hydrogen reaction was a catalyst precursor for arene hydrogenation—unlike analogous allylcobalt complexes. However, two of the complexes, the mono- and tris(phosphite) species, were catalysts for olefin hydrogenation. The crystal structure of $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]$ was established by an X-ray diffraction study. Square-pyramidal geometry is an accurate description of the inner coordination sphere. The unique axial site is occupied by the phosphite ligand.

Introduction

In earlier studies, we demonstrated a rich and diversified chemistry for allylcobalt[2,3] and allylrhodium[4] phosphite and phosphine complexes. Allylcobalt tris(phosphite) and tris(phosphine) complexes comprise a unique class of catalyst precursors that effect totally stereoselective hydrogenation of aromatic hydrocarbons.[3,6] In contrast, the allylrhodium bis(phosphite) complexes rapidly react with hydrogen to give propylene and polynuclear rhodium hydrides, $\{HRh[P(OR)_3]_2\}_x$, the resultant polynuclear hydrides are extremely active alkene and alkyne hydrogenation catalysts.[4,7] In extending this chemistry to iridium, we found diversity to prevail—the allyliridium chemistry was not analogous to that of either cobalt or rhodium.

Experimental Section

Reagents, Solvents, and General Procedures. All operations with air-sensitive materials were carried out in a Vacuum Atmosphere drybox under an argon atmosphere, in a conventional vacuum system or by using Schlenk technique. Trimethyl phosphite and 1,5-cyclooctadiene were purchased from Aldrich Chemical Co, Inc.; 1-hexene was purchased from Chem. Samp. Co.; tetraallyltin was purchased from ROC/RIC Corp. Iridium trichloride hydrate was obtained from Alfa Chemicals and Matthey Bishop, Inc. Prepurified hydrogen (99.95%) was purchased from Matheson & Co.

The 1,5-cyclooctadiene was purified by passing it down a neutral alumina column and degassing it prior to use or by vacuum distillation under nitrogen. 1-Hexene was dried by vacuum distillation from sodium benzophenone ketyl. Toluene, benzene, diethyl ether, and *n*-hexane were distilled from sodium benzophenone ketyl under nitrogen. The trimethyl phosphite was stored over sodium and vacuum distilled. Allyllithium[8a] and $[(1,5\text{-}COD)IRCl]_2$[9] were prepared according to literature methods. Tetraallyltin was vacuum distilled prior to use.

NMR spectra were obtained with a Varian Associates EM-390, Bruker-180, or Bruker HXS-360 spectrometer system. Proton chemical shifts were referenced to tetramethylsilane. Positive phosphorus chemical shifts were measured downfield from H_3PO_4. The volatile components from the attempted hydrogenation reactions of benzene and of 1-hexene were analyzed by gas chromatography[10] using a 12 ft × $^1/_8$ in. 15% OV-17 on Chromosorb W column and a 12 ft × $^1/_8$ in. 15% dimethylsulfolane on Chromosorb P column, respectively. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and the Analytical Laboratory at U.C.B.

Synthesis of $(\eta^3\text{-}C_3H_5)Ir(1,5\text{-}C_8H_{12})P(OCH_3)_3$. A brownish yellow C_3H_5Li (6.4 mmol) solution was prepared by the addition of $(C_3H_5)_4Sn$ (0.50 g, 1.8 mmol) to C_6H_5Li[8b] (0.54 g, 6.4 mmol) in diethyl ether (55 mL) followed by filtration of the resulting white $(C_6H_5)_4Sn$ precipitate after the mixture was stirred for 20 min.[8a]

To a cold mixture (at −78 °C, 2-propanol–dry ice bath) of $[(1,5\text{-}C_8H_{12})IrCl]_2$[9] (2.02 g, 3.0 mmol) in diethyl ether (20 mL) was added C_3H_5Li (6.4 mmol) in diethyl ether (55 mL) over a period of 20 min. The resulting orange-red mixture was stirred for an additional 40 min. Trimethyl phosphite (0.8 mL, 6.8 mmol) was syringed into the flask, resulting in a lightening of the color of the solution and subsequent precipitation of a white solid. Stirring at −78 °C was continued for 5 h, and the mixture was then warmed to the room temperature. Twelve hours later, the yellow mixture was filtered, and the filtrate was concentrated to an oil which was extracted with *n*-hexane. After concentration, the hexane extract was filtered and the filtrate was mixed with methanol (50 mL) and then set aside at −20 °C to give, after 1 day, white crystals.

---

† Dedicated to the memory of Rowland G. Pettit.

[1] For related allyl metal chemistry, see references 2–5.

[2] Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920.

[3] Stuhl, L. S.; Rakowski Dubois, M.; Hirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 2405.

[4] Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

[5] Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1978**, *17*, 2148.

[6] Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 556.

[7] (a) Brown, R. K.; Williams, J. M.; Fredrich, M. F.; Day, V. W.; Sivak, A. J.; Muetterties, E. L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2099. (b) Brown, R. K.; Williams, J. M.; Sivak, A. J.; Muetterties, E. L. *Inorg. Chem.* **1980**, *19*, 370. (c) Teller, R. G.; Williams, J. M.; Koetzle, T. F.; Burch, R. R.; Gavin, R. M.; Muetterties, E. L. *Ibid.* **1981**, *20*, 1806.

[8] (a) Prepared from C_6H_5Li[8b] and $(C_3H_5)_4Sn$: Seyferth, D.; Werner, M. A. *J. Org. Chem.* **1961**, *26*, 4797. (b) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* **1967**, *8*, 193.

[9] Heede, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

[10] Rakowski Dubois, M.; Hirsekorn, F. J.; Stuhl, L. S.; Muetterties, E. L. *Inorg. Chem.* **1976**, *15*, 2359.

0276-7333/82/2301-1562$01.25/0 © 1982 American Chemical Society

The crystals were collected and recrystallized from *n*-hexane or methanol at low temperature. Additional crystals were obtained by further concentrating the filtrate and cooling to −20 °C. Total yields varied from 1.375 (49%) to 1.115 g (40%): mp 97.5–99 °C; ^{1}H NMR (C_6D_6, 90 MHz, 30 °C) δ +4.65 (m, CH-allyl, 1), +3.55 (br s, CH-C_8H_{12}, 4), +3.20 (d, CH_3OP, J_{PH} = 11.4 Hz, 9), +2.15 (overlapping multiplets, CH_2-C_8H_{12} and CH_{syn}-allyl, 10), +1.42 (doublet of doublets, CH_{anti}-allyl, $J_{H_{anti}H_{CH}}$ = 8 Hz, $J_{H_{anti}P}$ = 21.6 Hz, 2); $^{31}P\{^1H\}$ NMR (toluene-d_8, 72.9 MHz, 25 °C) δ 125.3 (s); ^{1}H NMR (toluene-d_8, 180 MHz, −76 °C) δ 4.65 (m, CH-allyl, 1), 3.72, 3.3 (two broad multiplets, CH-C_8H_{12}, 4), 3.05 (d, CH_3OP, J_{PH} = 11.4 Hz, 9), 2.45 (m, $CH_{syn\text{-}allyl}$, 2), 2.0 (m, CH_2-C_8H_{12}, 8), δ 1.2 (doublet of doublets, $CH_{anti\text{-}allyl}$, $J_{H_{anti}H_{CH}}$ = 8 Hz, $J_{H_{anti}P}$ = 21.6 Hz, 2). Anal. Calcd for $C_{14}H_{26}IrO_3P$: C, 36.12; H, 5.63; Ir, 41.29; P, 6.65. Found: C, 35.90; H, 5.59; Ir 43.0; P, 6.94.

Synthesis of (η^1-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$]$_2$. (η^3-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$] (0.85 g, 1.83 mmol) was dissolved in a minimum amount of hexane and then treated with $P(OCH_3)_3$ (0.227 g, 1.83 mmol). The resulting solution was stirred for 10 min, allowed to stand overnight, and then cooled to −20 °C. White crystals were collected by filtration, washed with cold hexane, and dried under vacuum: 0.775 g, 72% yield; mp 91–92 °C; IR 1605 cm^{-1} (ν(C=C)); ^{1}H NMR (C_6D_6, 90 MHz, 30 °C) δ +6.20 (m, vinylic CH-allyl, 1), +4.75 (overlapping multiplets, vinyl CH_2-allyl, 2), +3.45 (overlapping multiplets, CH-$C_8H_{12}$and CH_3OP, 22), ~+2.3 (overlapping multiplets, CH_2-C_8H_{12} and methylene-allyl, 10); $^{31}P\{^1H\}$ NMR (toluene-d_8, 72.9 MHz, 25 and −68 °C) δ 109.0 (s). Anal. Calcd for $C_{17}H_{35}IrO_6P_2$: C, 34.63; H, 5.98; Ir, 32.6; P, 10.51. Found: C, 34.64; H, 6.01; Ir, 32.1; P, 10.81.

(η^1-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$]$_2$ can be synthesized by using the same procedure as that for (η^3-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$] with a 2:1 phosphite/iridium molar ratio. Repeated recrystallization gave analytically pure (η^1-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$]$_2$. Attempted sublimation of the bis(phosphite) led to loss of a phosphite ligand and formation of (η^3-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$].

Synthesis of (η^3-C_3H_5)Ir[$P(OCH_3)_3$]$_3$. A toluene solution (40 mL) of (η^3-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$] (0.65 g, 0.40 mmol) was treated with $P(OCH_3)_3$ (2 mL) and refluxed for 5 h. The resulting solution was concentrated to an oil which was extracted with hexane. The hexane solution was evaporated under vacuum. The solid residue was dissolved in diethyl ether, and the solution was filtered through Celite. A white waxy solid was obtained on evaporation of the ether: 0.63 g, 75% yield; mp 100 °C (darkens), 178–185 °C (decomposes to a brown oil)); ^{1}H NMR (C_6D_6, 90 MHz, 30 °C) δ +4.55 (m, CH-allyl, 1), +3.45 (m, CH_3OP, 27), +2.35 (d, CH_{syn}-allyl, $J_{H_{syn}H_{CH}}$ = 6 Hz, 2), +1.36 (quintet, H_A, $J_{H_{anti}H_{CH}} \approx J_{H_{anti}P} \approx$ 7 Hz, 2); $^{31}P\{^1H\}$ NMR (toluene-d_8, 72.9 MHz, −80 °C) AB_2 spectrum, δ_A 124.2, δ_B 121.3, and J_{AB} = 91.3 Hz; $^{31}P\{^1H\}$ NMR (toluene-d_8, 25 °C) δ 120.1. Anal. Calcd for $C_{12}H_{32}IrO_9P_3$: C, 23.80, H, 5.33; Ir, 31.74; P, 15.35. Found: C, 24.01; H, 5.31; Ir, 28.60; P, 15.89.

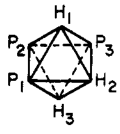
HIr[$P(OCH_3)_3$]$_4$. A hexane solution (~10 mL) of (η^3-C_3H_5)Ir[$P(OCH_3)_3$]$_3$ (0.44 g) with excess trimethyl phosphite was kept in a closed reaction tube and stirred under 1 atm of H_2 at room temperature for 9 days. The solvent and the remaining trimethyl phosphite were then removed under vacuum to yield a white waxy product: ^{1}H NMR (C_6D_6, 90 MHz, 35 °C) δ 3.5 (m, CH_3OP, 36), −14.2 (quintet $J_{P\text{-}H}$ = 18.5 Hz, 1); IR (Nujol) Ir–H, 2055 cm^{-1}. $^{31}P\{H_{OCH_3}\}$ NMR (toluene-d_8, 72.9 MHz, 25 °C) δ 125.0 (d, $J_{P\text{-}H}$ = 18.5 Hz). Anal. Calcd for $C_{12}H_{37}IrO_{12}P_4$: C, 20.90; H, 5.42; P, 17.97. Found: C, 21.17; H, 5.27; P, 17.96.

(η^3-C_3H_5)Ir[$P(OCH_3)_3$]$_3$ Reaction with Hydrogen in Benzene and with $P(OCH_3)_3$. (η^3-C_3H_5)Ir[$P(OCH_3)_3$]$_3$ (0.136 g, 0.224 mmol) was dissolved in benzene (2 mL, 0.224 mmol) contained in a reaction tube fitted with a Kontes stopcock. The tube was cooled to −196 °C, evacuated, and filled with H_2 (76 cmHg). The solution was warmed to room temperature and stirred for 48 h. During this time, the solution gradually turned yellow. The volatile components were collected by vacuum distillation on a vacuum line, and the remaining yellow oil was dissolved in toluene-d_8 for NMR spectrum. The ^{1}H NMR of the yellow oil indicated three hydride species were present. *fac*-H_3Ir[$P(OCH_3)_3$]$_3$ was the major species: $^{31}P\{^1H\}$ NMR (toluene-d_8, 72.9 MHz) δ 122.2 (s); ^{1}H NMR (toluene-d_8, 360 MHz, hydride region) AA′A″XX′X″ spectrum, δ −12.55 to −13.60. Minor species were HIr[$P(OCH_3)_3$]$_4$ (NMR spectrum see above) and *mer*-H_3Ir[$P(OCH_3)_3$]$_3$: $^{31}P\{^1H\}$ (toluene-d_8, 72.9 MHz) AB_2 spectrum, δ_A 126.8, δ_B 122.9, J = 33.4 Hz; ^{1}H NMR (toluene-d_8, 360 MHz hydride region) $\delta_{H_1} = \delta_{H_3}$ −12.41, δ_{H_2} −14.03. The remaining coupling constants for the meridianal isomer were determined from the ^{31}P and ^{1}H NMR spectra: $J_{H_1H_2} = J_{H_3H_2}$ = 4.6 Hz; $J_{P_1H_2} = J_{P_3H_2}$ = 191 Hz; $J_{P_2H_2}$ = 166 Hz; $J_{P_2H_1} = J_{P_2H_3}$ = 150 Hz; $J_{P_1H_1} = J_{P_1H_3} = J_{P_3H_1} = J_{P_3H_3}$ = 187 Hz; labeled structure 1. Analysis of the volatile reaction components by gas chromatography showed the absence of any significant amount of cyclohexane.

Table I. 1-Hexene–H_2 Reactions (25 °C)

catalyst	time, h	% of 1-hexene conversn to products
(η^3-C_3H_5)Ir(η^4-C_8H_{12})-[$P(OCH_3)_3$]^b	7^d	hexane (90%), 2- and 3-hexenes (8%)
(η^1-C_3H_5)Ir(η^4-C_8H_{12})-[$P(OCH_3)_3$]$_2$^{b}	24	<1% hexane
(η^3-C_3H_5)Ir[$P(OCH_3$]$_3$^{b}	14	>99% hexane
HIr[$P(OCH_3)_3$]$_4$^{c}	22	none
H_3Ir[$P(OCH_3)_3$]$_3$ *fac*, *mer*^{a,b}	24	hexane (68%), 2- and 3-hexenes (30%)

^{a} Contaminated with a small amount of HIr[P)$OCH_3)_3$]$_4$. ^{b} 0.11 mmol. ^{c} 0.09 mmol. ^{d} 5.6 mmol of 1-hexene; all other experiments with 8.0 mmol of 1-hexene.



1

In contrast to the (η^3-C_3H_5)Rh[$P(OCH_3)_3$]$_3$ system, a toluene solution of (η^3-C_3H_5)Ir[$P(OCH_3)_3$]$_3$ with excess $P(OCH_3)_3$ showed no NMR (^{1}H) evidence for the presence of (η^1-C_3H_5)Ir[$P(OCH_3)_3$]$_4$ or for fast exchange.

Catalytic Reactions. Following the procedure, the precise reaction conditions and reagent amounts, and the analytical procedure described by Rakowski et al.,[10] the hydrogenation of benzene with the three allyliridium complexes was examined. Over reaction periods of ~1 day, there was no detectable hydrogenation of benzene. A similar procedure was employed for 1-hexene hydrogenation using 8.0 mmol of hexene and 0.11–0.09 mmol of iridium complex. Results are presented in Table I.

X-ray Crystallographic Study[11] of (η^3-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$], 4. Large, well-shaped colorless, single crystals of (η^3-C_3H_5)Ir(1,5-C_8H_{12})[$P(OCH_3)_3$], 4, were obtained from hexane solution. They are, at 20 ± 1 °C, orthorhombic with a = 8.929 (2) Å, b = 13.885 (2) Å, c = 25.677 (4) Å, V = 3183.2 (8) Å^3, and Z = 8 (μ_a(Mo $K\bar{\alpha}$)[12a] = 9.00 nm^{-1}; d_{calcd} = 1.94g cm^{-3}). The systematically absent reflections in the diffraction pattern were those for the uniquely determined centrosymmetric space group *Pbca*—D_{2h}^{15} (No. 61).[13]

Intensity measurements were made on a Nicolet P$\bar{1}$ autodiffractometer using 0.90° wide ω scans and a graphite-monochromated Mo $K\bar{\alpha}$ radiation for a specimen having the shape of a rectangular parallelepiped with dimensions of 0.31 × 0.40 × 0.46 mm. This crystal was sealed under N_2 in a thin-walled glass capillary and mounted on a goniometer head with its longest dimension nearly parallel to the phi axis of the diffractometer. A total of 4384 independent reflections having $2\theta_{MoK\bar{\alpha}} < 58.70$ (the equivalent of 1.2 limiting Cu $K\bar{\alpha}$ spheres) were measured in three concentric shells of 2θ. A scanning rate of 4°/min was used to measure intensities for reflections having $3° < 2\theta \leq 43°$ and rates of 3°/min and 2°/min were used for those having $43° \leq 2\theta < 55°$ and $55° \leq 2\theta < 58.7°$, respectively. The data collection and reduction procedures which were used are described in ref 14; the

---

(11) See paragraph at end of paper regarding supplementary material.

(12) (a) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 55–56. (b) *Ibid.*, pp 99–101. (c) *Ibid.*, pp 149–150.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I, p 150.

(14) Wreford, S. S.; Kouba, J. K.; Kirner, J. F.; Muetterties, E. L.; Tavanaiepour, I.; Day, V. W. *J. Am. Chem. Soc.* 1980, *102*, 1558.

scan width and stepoff for background measurements were both 0.90°. The intensity data were corrected empirically for absorption effects using psi scans for ten reflections having 2θ between 5° and 35° (the relative transmission factors ranged from 0.654 to 1.000).

The structure was solved by using the "heavy-atom" technique. Unit-weighted full-matrix least-squares refinement which utilized anisotropic thermal parameters for all non-hydrogen atoms converged to R_1(unweighted, based on F)[15] = 0.040 and R_2(weighted, based on F)[15] = 0.046 to 1438 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. When a difference Fourier calculated at this pointed failed to give reasonable positions for hydrogen atoms, positions for hydrogen atoms of the allyl and cyclooctadiene ligands were calculated by using idealized sp^2 or sp^3 hybridization for the carbon atoms and a C–H bond length of 0.95 Å.

The hydrogen atom parameters were not varied during least-squares refinement cycles; the idealized positions were periodically recalculated. Unit-weighted refinement cycles with the more complete ($2\theta_{\mathrm{MoK}\bar{\alpha}} < 58.7°$) data set which varied parameters for anisotropic non-hydrogen atoms but not those for isotropic hydrogen atoms, gave $R_1 = 0.044$ and $R_2 = 0.048$ for 2822 reflections. The final cycles of empirically weighted[16] full-matrix least-squares refinement gave $R_1 = 0.042$ and $R_2 = 0.054$ for 2822 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 58.7°$ and $I > 3\sigma(I)$. Since a careful comparison of final $|F_o|$ and $|F_c|$ values indicated the absence of extinction effects, extinction corrections were not made.

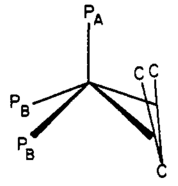
All structure factor calculations employed recent tabulations of atomic form factors[12b] and anomalous dispersion corrections[12c] to the scattering factors of the Ir and P atoms. All calculations were performed on a Data General Eclipse S-200 computer equipped with 64K of 16-bit words, a floating point processor for 32- and 64-bit arithmetic, and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Co.

Results and Discussion

Synthesis and Chemistry. Allyliridium η^4-1,5-cyclooctadiene was synthesized and used as an intermediate for the preparation of the allyliridium phosphite complexes. This cyclooctadiene complex proved to be too thermally reactive for conventional isolation procedures and was generated from allyllithium and $[\mathrm{ClIr(1,5\text{-}COD)}]_2$ at low temperatures (−78 °C) and then was directly reacted with trimethyl phosphite. By way of comparison, the analogous allylrhodium complex was isolable at 20 °C and was purified by vacuum sublimation at 20 °C although this complex slowly decomposed in the solid state at 20 °C.[4]

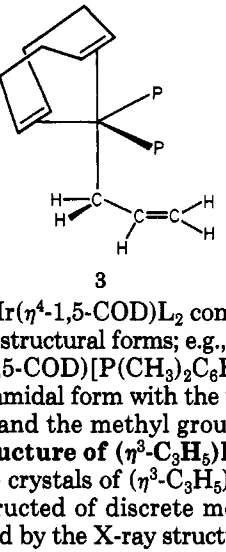
Whereas $(\eta^3\text{-}C_3H_5)Rh(\eta^4\text{-}1,5\text{-}COD)$ reacted nearly quantitatively with 2 and 3 equiv of a phosphite of phosphine (L) to form $(\eta^3\text{-}C_3H_5)RhL_2$ and $(\eta^3\text{-}C_3H_5)RhL_3$, respectively,[4] the iridium complex reacted with trimethyl phosphite at −78 °C to form $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]$. Addition of a second equivalent of trimethyl phosphite did not lead to cyclooctadiene displacement but to the formation of the σ-allyl complex, $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]_2$. Cyclooctadiene was displaced only on reaction of the bis(phosphite) complex with excess trimethyl phosphite at ~90 °C. Another measure of the robust iridium–diene bonding was the conversion of $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]_2$, on warming under vacuum, to the mono(phosphite) complex, $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]$, rather than to a species such as $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_2$ which in the rhodium system[4] is an isolable and quite thermally stable complex.

Solution-State Structure. The structures of the three allylrhodium complexes are reasonably well-defined by spectroscopic and crystallographic information. ^1H and ^{31}P NMR data and analogy to the cobalt system support structure 2 for $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$. A crystallographic study established structural form 2 for $(\eta^3$-cyclooctenyl)$Co[P(OCH_3)_3]_3$.[17] Both the iridium complex and the $\eta^3\text{-}C_3H_5Co$ analogue[2] are stereochemically nonrigid and have A_3 and AB_2 fast and slow-exchange limiting $^{31}P\{^1H\}$ spectra. The only substantive difference between the two complexes is in the exchange barrier: the AB_2 spectrum was observed below −120 °C and below ~−70 °C for the cobalt and iridium complexes, respectively. Since the ^{31}P chemical shift for the axial phosphorus atom (P_A) in $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$ and for the single phosphorus atom in $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)P(OCH_3)_3$ are very similar, a square-pyramidal form with an axial phosphite ligand is a reasonable formulation for the latter complex in the solution state. A crystallographic study of this complex, described below, established such a square-pyramidal stereochemistry for the solid state.



2

The $^{31}P\{^1H\}$ spectrum of $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-}COD)[P(OCH_3)_3]_2$ consisted of a singlet (to −70 °C) with a chemical shift very different from those of the other two allyliridium complexes. Structure 3 is proposed for this η^1-allyl complex. Analogous $XIr(\eta^4\text{-}1,5\text{-}COD)L_2$ complexes have been shown to have such structural forms; e.g., a crystallographic study[18] of $CH_3Ir(1,5\text{-}COD)[P(CH_3)_2C_6H_5]_2$ established a near trigonal-bipyramidal form with the phosphine ligands at equatorial sites and the methyl group at an axial site.



3

Solid-State Structure of $(\eta^3\text{-}C_3H_5)Ir[\eta^4\text{-}1,5\text{-}COD]P(OCH_3)_3$, 4. Single crystals of $(\eta^3\text{-}C_3H_5)Ir[\eta^4\text{-}1,5\text{-}COD]P(OCH_3)_3$ are constructed of discrete mononuclear metal complexes as defined by the X-ray structural analysis. The mononuclear complex is illustrated in Figure 1. Presented in Tables II and III[20] are the final atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms, respectively. Idealized atomic coordinates for hydrogen atoms of the allyl and cyclooctadiene ligands are listed in Table IV.[20] Bond distances and angles are presented in Tables V and VI,[20] respectively, for the coordination group atoms and for the ligands. The numbering protocol for

---

(15) The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

(16) Empirical weights were calculated from the equation $\sigma\sum_0^3 a_n|F_o|^n = 3.50 - 1.30 \times 10^{-2}|F_o| + 1.34 \times 10^{-4}|F_o|^2 - 1.33 \times 10^{-7}|F_o|^3$ the a_n being coefficients derived from the least-squares fitting $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$, where the F_c values were calculated from the fully refined model by using unit weighting and the $I > 3\sigma(I)$ rejection criterion.

(17) Tau, K. D.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Inorg. Chem.* **1981**, *20*, 1237.

(18) Churchill, M. R.; Bezman, S. A. *Inorg. Chem.* **1972**, *11*, 2243.

(19) The propylene was hydrogenated by hydridoiridium complexes present in these solutions.

(20) See supplementary material.

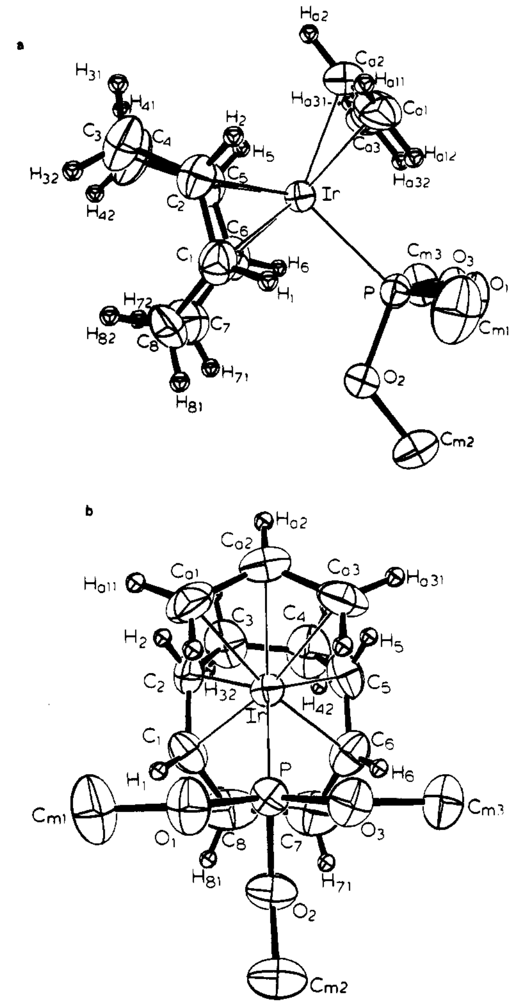


Figure 1. Perspective ORTEP drawings of the $(\eta^3\text{-}C_3H_5)Ir(1,5\text{-}C_8H_{12})[P(OCH_3)_3]$ molecule, 4, viewed: (a) nearly perpendicular and (b) parallel to the pseudo mirror plane which would ideally contain Ir, P, O_2, C_{m2} and C_{a2}. All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density; hydrogen atoms for the allyl and cyclooctadiene ligands are shown in their idealized positions with arbitrarily sized spheres for purposes of clarity. Methyl hydrogen atoms of the phosphite ligand are not shown.

Table II. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $(\eta^3\text{-}C_3H_5)Ir(1,5\text{-}C_8H_{12})[P(OCH_3)_3]$[a]

atom[b]	10^4x	10^4y	10^4z
Ir	1084.9 (4)	1077.6 (2)	1120.8 (1)
P	500 (3)	47 (2)	1779 (1)
O_1	−1083 (9)	−527 (6)	1777 (3)
O_2	1719 (9)	−789 (5)	1875 (3)
O_3	187 (8)	460 (5)	2355 (3)
C_{m1}	−1448 (17)	−1127 (11)	1325 (6)
C_{m2}	1532 (17)	−1490 (9)	2304 (5)
C_{m3}	1357 (12)	1042 (9)	2598 (4)
C_{a1}	−1259 (13)	1296 (10)	924 (5)
C_{a2}	−504 (14)	2169 (9)	998 (4)
C_{a3}	32 (15)	2301 (8)	1505 (5)
C_1	1947 (13)	−39 (8)	608 (4)
C_2	1584 (13)	778 (8)	316 (4)
C_3	2712 (17)	1434 (10)	72 (5)
C_4	3677 (17)	1986 (11)	465 (6)
C_5	3121 (13)	1889 (9)	1016 (5)
C_6	3430 (12)	1099 (10)	1340 (5)
C_7	4289 (16)	251 (12)	1155 (7)
C_8	3562 (18)	−328 (12)	725 (5)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1.

Table V. Bond Lengths, Polyhedral Edge Lengths, and Bond Angles Subtended at the Ir(I) Ion in Crystalline $(\eta^3\text{-}C_3H_5)Ir(1,5\text{-}C_8H_{12})[P(OCH_3)_3]$[a]

parameter[b]	value	parameter[b]	value
	Distances, Å		
Ir–P	2.276 (2)	$C_{a2}\cdots C_2$	3.206 (16)
		$C_{a2}\cdots C_5$	3.260 (17)
Ir–C_{a1}	2.174 (11)		
Ir–C_{a3}	2.178 (11)	$P\cdots C_{a1}$	3.209 (13)
		$P\cdots C_{a2}$	3.675 (12)
Ir–C_{a2}	2.100 (12)	$P\cdots C_{a3}$	3.235 (11)
Ir–C_1	2.175 (11)	$P\cdots C_1$	3.276 (11)
Ir–C_2	2.154 (9)	$P\cdots C_6$	3.201 (12)
Ir–C_5	2.156 (12)		
Ir–C_6	2.168 (11)	$P\cdots C_{ga}$[c]	3.221 (-)
Ir–C_{ga}[c]	1.892 (-)	$P\cdots C_{g12}$[c]	3.594 (-)
		$P\cdots C_{g56}$	3.545 (-)
Ir–C_{g12}[c]	2.049 (-)		
Ir–C_{g12}[c]	2.044 (-)	$C_{ga}\cdots C_{g12}$[c]	3.474 (-)
		$C_{ga}\cdots C_{g56}$	3.492 (-)
$C_{a1}\cdots C_2$	3.065 (16)		
$C_{a3}\cdots C_5$	3.084 (18)	$C_{g12}\cdots C_{g56}$[c]	2.763 (-)
	Bond Angles, Deg		
$PIrC_{ga}$[c]	100.8 (–)	$C_{a1}IrC_{a2}$	38.2 (5)
		$C_{a3}IrC_{a2}$	38.1 (5)
$PIrC_{g12}$[c]	112.3 (-)	C	
$PIrC_{g56}$[c]	110.1 (-)	C_1IrC_2	37.6 (4)
		C_5IrC_6	37.9 (4)
$C_{ga}IrC_{g12}$[c]	123.6 (-)		
$C_{ga}IrC_{g56}$	125.0 (-)	C_1IrC_6	79.9 (4)
		C_2IrC_5	78.9 (4)
$C_{g12}IrC_{g56}$[c]	84.9 (-)		
		C_1IrC_5	89.9 (4)
$C_{a1}IrC_{a3}$	65.2 (5)	C_2IrC_6	93.0 (4)

[a] Numbers in parentheses are the estimated standard deviation for the last significant digit. [b] Atoms are labeled in agreement with Tables II–IV and Figure 1. [c] The subscript g denotes center of gravity.

atoms in 4 is given in ref 21.

The iridium atom in 4 is within bonding distance of the three allylic carbon atoms, the four olefinic carbon atoms of the cyclooctadiene ligand, and the phosphite phosphorus atom. Generally, $(\eta^3\text{-allyl})$metal complexes with three other ligands adopt a coordination geometry than can be represented ideally as five-coordinate with the allyl ligand occupying two-coordinate sites.[22] The iridium complex conforms to the general rule and has a polytopal form analogous to that of $(\eta^3\text{-cyclooctenyl})Co[P(OCH_3)_3]_3$,[23] **5**, and $(\eta^3\text{-allyl})Co(CO)_2[P(C_6H_5)_3]$,[24] **6**. The allyliridium complex, 4, is described best as square pyramidal with the allyl ligand spanning adjacent basal sites as in 5 and 6 and with an apical phosphite phosphorus atom. Maximal possible symmetry is C_s-*m* which is approached closely in 4: atoms Ir, P, O_2, C_{m2}, C_{a2}, and H_{a2}, which define the *idealized* mirror plane, are coplanar to within 0.03 Å and their least-squares mean plane[25a] makes a dihedral angle

---

(21) The labeling scheme used to designate atoms of 4 is as follows. Atoms of the allyl ligand are designated by a subscripted a and methyl carbon atoms of the trimethyl phosphite ligand by a subscripted m. Non-hydrogen atoms of the same type within each ligand are distinguished from each other by a numerical subscript to the appropriate atomic symbol. Hydrogen atoms of the allyl and cyclooctadiene ligands carry the same subscripts as the carbon atoms to which they are covalently bonded as well as a final numerical subscript to distinguish (when necessary) between hydrogens bonded to the same carbon.

(22) Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107.

(23) Thompson, M. R.; Day, V. W.; Tau, K. D.; Muetterties, E. L. *Inorg. Chem.* **1981**, *20*, 1237.

(24) Rinze, P. V.; Muller, U. *Chem. Ber.* **1979**, *112*, 1973.

of 91.3° with that[25b] of a basal coordination plane[26] defined by the terminal allylic carbon atoms (C_{a1} and C_{a3}) and the midpoints of the cyclooctadiene olefinic carbon atoms (C_{g12} and C_{g56}). The plane defined by the three allyl carbon atoms[25c] generates a dihedral angle of 90.1° with the aforementioned idealized mirror plane. Configurationally, the allylic ligand in **4** is analogous to that in **5** and **6** and has a staggered orientation with respect to the triangular coordination face of the square pyramid, a face defined in **4** by P, C_{ag12}, and C_{ag23}. This is the electronically[27] and sterically preferred orientation.

An examination of nonbonded intramolecular contacts for **4** indicates a congested coordination sphere. There are numerous interligand $P\cdots C$, $C\cdots C$, $P\cdots H$, $C\cdots H$, and $H\cdots H$ contacts, substantially less than their respective van der Waals values[28] of 3.60, 3.40, 3.10, 2.90, and 2.40 Å: $P\cdots C_{a1}$ = 3.209 (13) Å; $P\cdots C_{a3}$ = 3.24 (1) Å; $P\cdots C_1$ = 3.28 (1) Å; $P\cdots C_6$ = 3.20 (1) Å; $C_2\cdots C_{a1}$ = 3.07 (2) Å; $C_5\cdots C_{a3}$ = 3.08 (2) Å; $C_2\cdots C_{a2}$ = 3.21 (2) Å; $C_5\cdots C_{a2}$ = 3.26 (2) Å; $P\cdots H_{a12}$ = 2.49 (-) Å; $P\cdots H_{a32}$ = 2.52 (-) Å; $P\cdots H_1$ = 2.82 (-) Å; $P\cdots H_6$ = 2.74 (-) Å; $C_{a1}\cdots H_2$ = 2.39 (-) Å; $C_{a3}\cdots H_5$ = 2.40 (-) Å; $H_2\cdots H_{a11}$ = 2.17 (-) Å; and $H_5\cdots H_{a31}$ = 2.19 (-) Å. These short nonbonded contacts clearly indicate that the solid-state structure of **4** shown in Figure 1 represents a low-energy conformation with an efficient packing of the ligands within the iridium coordination sphere. Thus, the allylic ligand is oriented with C_{a2} and its hydrogen atom directed away from the phosphorus atom and nestled between cyclooctadiene olefinic hydrogen atoms H_2 and H_5. The phosphite phosphorus atom is similarly situated in a "pocket" surrounded by cyclooctadiene olefinic hydrogen atoms H_1 and H_6 and allyl hydrogen atoms H_{a12} and H_{a13}. Furthermore, the O_2 methoxy group is directed away from the allyl ligand to a position above the cyclooctadiene ring. Cyclooctadiene hydrogen atom H_2 is directed between allyl hydrogen atoms H_{a11} and H_{a2}; H_5 is directed between H_{a31} and H_{a2}. Summarily, the orientation of a given ligand on the coordination sphere of **4** is highly dependent on the relative orientation of the others.

Since the cyclooctadiene ligand would be expected to be the most inflexible of those present in **4**, it should be informative to make detailed comparisons between the coordination groups of **4** and **5**. The ligand complement in **4** can be derived from that of **5** in the cobalt analogue by replacing the η^3-bonded cyclooctenyl ligand with an unsubstituted allyl ligand and the two "basal" trimethyl phosphite ligands by the bidentate cyclooctadiene ligand. Sterically, the substitution of allyl for cyclooctenyl would be expected to reduce congestion between the η^3-allyl group and the apical phosphite ligands. The replacement of the two "basal" phosphite ligands by a more rigid bidentate cyclooctadiene ligand would be expected to decrease the "basal" L–M–L (L_2 = cyclooctadiene in **4** and L = phosphite in **5**) angles and increase congestion between these two L coordination sites and the remaining three. The net effect of these coordination sphere alterations should thus be smaller P_{apical}–M–C_{ga}[26] and "basal" L–M–L angles in **4** than in **5** and larger P_{apical}–M–L_{basal} and C_{ga}–M–L angles in **4** than in **5**. The following averaged[29] values for ligand bond angles subtended at the metals in **4** and **5** are in full agreement with these expectations: P_{apical}–M–C_{ga} = 100.8° in **4** and 116.5° in **5**; "basal" L–M–L = 84.9° in **4** and 97.4° in **5**; P_{apical}–M–L_{basal} = 111.2 (-, 11, 11, 2) in **4** and 104.9 (1, 14, 14, 2)°[29] in **5**; and C_{ga}–M–L = 124.3 (-, 7, 7, 2)° in **4** and 115.4 (-, 10, 10, 2)° in **5**. Thus, the steric demands of the relatively bulky cyclooctadiene ligand manifest themselves in **4** even though the metal diameter is considerably larger (>0.20 Å) than in **5**.

The ~0.15 Å elongation of the M–C_{a2} and M–P_{apical} bonds in **4** relative to **5**[23] can probably be attributed to the larger size of the metal atom in **4**. The relatively small (only 0.057-Å) differences in M–C_{a1} and M–C_{a3} distances between **4** and **5** might reflect steric elongation of these bonds in **5** due to short nonbonded repulsions of the cyclooctenyl ligand with the axial phosphite ligand. Generally, the parameters for the coordinated trimethyl phosphite and cyclooctadiene ligands are comparable to those reported in analogous complexes.[23,30-32] There are no intermolecular contacts which are substantially less than the respective van der Waals value.[28]

Catalytic Chemistry. None of the three allyliridium complexes was a catalyst precursor for arene hydrogenation although both (η^3-allyl)iridium complexes were quite active catalyst precursors for olefin hydrogenation. The allyliridium bond was rapidly cleaved in these hydrogen reactions a feature common to the allylcobalt[6] and allylrhodium[4] phosphite complexes. Hydrogen, in the presence and absence of a reducible substrate, effected an irreversible cleavage of the allyliridium bond to give propylene (initially[19]) and a series of iridium hydride complexes. The tris(phosphite), **2**, primarily formed the facial and meridianal isomers of $H_3Ir[P(OCH_3)_3]_3$ with the facial isomer the dominant one. A small but significant coproduct was $HIr[P(OCH_3)_3]_4$; hence stoichiometry requires that another iridium complex was formed, but none was spectroscopically detected. Since $H_3Ir[P(OCH_3)_3]_3$ and $HIr[P(OCH_3)_3]_4$ are stable complexes, the formation of the latter requires phosphite ligand dissociation, probably in the allyliridium hydride intermediate, as a process competitive with the allyl cleavage reaction; similar chemistry was operative in the hydrogen cleavage of the allyl–rhodium bond in the analogous rhodium complexes.[4]

Cyclooctane and the facial and meridianal isomers of $H_3Ir[P(OCH_3)_3]_3$ were formed in the reaction of $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-}1,5\text{-COD})[P(OCH_3)_3]_2$ and hydrogen in benzene solution; another unidentified hydride (see below) was also formed in this reaction. Curiously, this bis(phosphite) complex did not significantly react with hydrogen when the reaction was effected with 1-hexene as the solvent.

---

[25] The least-squares mean planes for the following groups of atoms in **4** are defined by the equation: $aX + bY + cZ = d$, where X, Y, and Z are orthogonal coordinates measured along $\vec{\mathbf{a}}$, $\vec{\mathbf{b}}$, and $\vec{\mathbf{c}}$, respectively of the crystal system: (a) Ir, P, O_2, C_{m2}, C_{a2}, and H_{a2} (coplanar to within 0.03 Å), a = 0.493, b = 0.593, c = 0.637, d = 3.192; (b) C_{a1}, C_{a3}, C_{g12}, and C_{g56}[26] (coplanar to within 0.03 Å), a = −0.063, b = −0.724, c = 0.687, d = 0.370; (c) C_{a1}, C_{a2}, and C_{a3}, a = −0.862, b = 0.438, c = 0.255, d = 2.363.

[26] C_{ga} is used to represent the center-of-gravity for the three carbon atoms of the allyl ligand. C_{g12} and C_{g56} are used to designate the midpoints of the cyclooctadiene olefinic $C_1{=}C_2$ and $C_5{=}C_6$ bonds, respectively.

[27] Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496.

[28] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960, p 260.

[29] The first number in parenthesis following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

[30] (a) Day, V. W.; Abdel-Meguid, S. S.; Dabestani, S.; Thomas, M. G.; Pretzer, W. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1976**, *98*, 8289. (b) Kulzick, M.; Price, R. T.; Muetterties, E. L.; Day, V. W. *Organometallics*, **1982**, *1*, 1256.

[31] (a) Goh, L.-Y.; D'Aniello, M. J., Jr.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* **1979**, *18*, 192. (b) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 188. (c) Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657. (d) Meier, E. B.; Burch, R. R.; Muetterties, E. L.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 2661.

[32] Day, C. S.; Day, V. W.; Shaver, A.; Clark, H. C. *Inorg. Chem.* **1981**, *20*, 2188.

Under these conditions, less than 1% of the 1-hexene solvent was converted to *n*-hexane in a 24-h period at 25 °C.

Hydrogen reacted with a benzene solution of $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-COD})[P(OCH_3)_3]$ to form propane, cyclooctane, and a new iridium complex. The ^1H NMR spectrum of this hydride consisted of a phosphite methoxy doublet resonance and a broad complex multiplet in the hydride region. All attempts to isolate the hydride in crystalline form failed; the hydride appeared to be a multinuclear iridium hydride, possibly analogous to the $[HRhP(OR)_3]_x$[4] complexes.

Both $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$ and $(\eta^3\text{-}C_3H_5)Ir(\eta^4\text{-1,5-COD})[P(OCH_3)_3]$ were active catalyst precursors for 1-hexene hydrogenation to hexane (Table I). Isomerization of the 1-hexene to the *cis*- and *trans*-2-hexene and *cis*- and *trans*-3-hexene isomers was a significant (~10%) competing process to olefin hydrogenation with the latter complex but not with the former (<1% isomerization). The mixture of $(\eta^3\text{-}C_3H_5)Ir[P(OCH_3)_3]_3$–hydrogen cleavage products also catalyzed 1-hexene hydrogenation and isomerization. In separate experiments with the hydrides derived from the allyliridium complex, it was established that the $H_3Ir[P(OCH_3)_3]_3$ isomers are active species in the reaction system. However, the catalytic activity of the trihydrides was lower than for the parent allyl complex, and these trihydrides, unlike the allyl precursor complex, were, in the presence of hydrogen, active olefin isomerization catalysts. $HIr[P(OCH_3)_3]_4$, like the cobalt[2] analogue, was not detectably active as a catalyst for olefin hydrogenation.

Generally, the presence of a reducible substrate like 1-hexene appeared to "inhibit" the reductive hydrogenation of the organic ligands in the allyliridium complexes. As noted above, $(\eta^1\text{-}C_3H_5)Ir(\eta^4\text{-1,5-COD})[P(OCH_3)_3]_2$ was not an active catalyst for either olefin isomerization or hydrogenation. The presence of 1-hexene literally blocked (over a 24-h reaction period) the hydrogenation of the allyl and cyclooctadiene ligands in the bis(phosphite) complex, whereas this process was relatively fast in the absence of an olefin (benzene solution). Presumably, the hexene captured a coordinately unsaturated intermediate, an intermediate that reacts with hydrogen to effect, ultimately, the hydrogenation of the hydrocarbon ligands. The effect of the presence of a reducible substrate on the rate of allyl–metal bond cleavage was also observed for (trialkyl phosphite)allylcobalt complexes; the rate was substantially higher in cyclohexane solution than in benzene (a reducible substrate for these cobalt complexes).[3,6,10]

Acknowledgment. This research was supported by the National Science Foundation and by a generous loan of iridium chloride by Johnson Matthey, Inc. A. C. Sievert and R. R. Burch assisted in the NMR measurements. NMR measurements at 360 MHz were performed at the Stanford Magnetic Resonance Laboratory with support from NSF Grant no. GP23633 and NIH Grant No. RR00711. V.W.D. acknowledges the Camille and Henry Dreyfus Foundation for support in the form of a Teacher-Scholar Award.

Registry No. 4, 82932-72-7; $(\eta^1\text{-}C_3H_5)Ir(COD)[P(OCH_3)_3]_2$, 82932-73-8; $(\eta^3\text{-}C_3H_5)IR[P(OCH_3)_3]_3$, 82951-07-3; $HIr[P(OCH_3)_3]_4$, 82932-74-9; *lac*-$H_3Ir[P(OCH_3)_3]_3$, 82932-75-0; *mer*-$H_3Ir[P(OCH_3)_3]_3$, 82977-26-2; 1-hexene, 592-41-6.

Supplementary Material Available: Crystal structure analysis report, structure factor amplitude table, and Tables III, IV, and VI for anisotropic thermal parameters, idealized atomic coordinates for hydrogen atoms, and ligand bond lengths and angles, respectively, in 4 (22 pages). Ordering information is given on any current masthead page.

Formation and Molecular Structure of (η^4-Tetraphenylcyclobutadiene)dicarbonylnitrosylmanganese[†]

Marvin D. Rausch,*[1a] Bruce H. Edwards,[1a] Jerry L. Atwood,[1b] and Robin D. Rogers[1b]

Departments of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, and University of Alabama, University, Alabama 35486

Received July 23, 1982

A reaction between tetracarbonylnitrosylmanganese and diphenylacetylene in refluxing toluene solution has produced the title compound, $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$, in low yield. The product, which represents the first cyclobutadiene derivative of a group 7B metal, has been characterized by infrared and mass spectral data as well as by a single-crystal X-ray diffraction study. $[\eta^4\text{-}(C_6H_5)_4C_4](CO)_2(NO)Mn$ crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters $a = 8.921$ (2) Å, $b = 18.775$ (8) Å, $c = 14.056$ (5) Å, $\beta = 92.27$ (3)°, and $D_{\text{calcd}} = 1.40$ g cm^{-3} for $Z = 4$. Least-squares refinement gave a final R value of 0.041 using 878 independent observed reflections. The tetraphenylcyclobutadiene ligand is η^4 coordinated to the Mn atom at an average Mn–C distance of 2.11 (2) Å. The four atoms of the cyclobutadiene ring are planar to within 0.001 Å. Two of the X–O (X = N or C) ligands are disordered.

Introduction

The formation, structure, and properties of cyclobutadiene have fascinated both synthetic and theoretical chemists for over a century.[2] In recent years, organometallic chemistry has played a significant role in the development of this topic. Thus, while cyclobutadiene itself is highly unstable, Longuet-Higgins and Orgel[3] proposed in 1956 that cyclobutadiene might form stable

---

[†] Dedicated to the late Professor Rowland Pettit, a brilliant and dedicated chemist whose enthusiasm for research was equaled only by his friendship for his fellow colleagues.

(1) (a) University of Massachusetts. (b) University of Alabama.
(2) Maier, G. *Angew. Chem., Int. Ed. Engl.* 1974, *13*, 425.
(3) Longuet-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* 1956, 1969.

0276-7333/82/2301-1567$01.25/0 © 1982 American Chemical Society