Iridium η^4-1,5-Cyclooctadiene and 1,2-η^2,6-σ-Cycloocta-1,4-dienyl Complexes. Deprotonation of Coordinated 1,5-Cyclooctadiene by Strong and Weak Bases

Anne M. Gull, Phillip E. Fanwick,[†] and Clifford P. Kubiak[*]

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

The reaction of [Ir(η^4-1,5-cyclooctadiene)Cl]$_2$ with 2 equiv of triphos [(Ph$_2$PCH$_2$CH$_2$)$_2$PPh] in methylene chloride yields [Ir(triphos)(η^4-1,5-cyclooctadiene)][Cl] (1), which upon reaction with various bases [KOH, NaOCH$_3$, NaOC$_6$H$_5$, NaOC$_6$H$_4$-p-CH$_3$, NaOC$_6$H$_4$-p-C(CH$_3$)$_3$, N(C$_2$H$_5$)$_3$, pyridine, N,N,N',N'-tetramethyl-1,8-naphthalenediamine (Proton Sponge)] in tetrahydrofuran solutions affords the neutral deprotonated complex, Ir(triphos)(1,2-η^2,6-σ-cycloocta-1,4-dienyl) (2). X-ray structure determinations of 1 and 2 were undertaken. Complex 1 crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.165(2)$ Å, $b = 10.791(2)$ Å, $c = 23.488(2)$ Å, $V = 3843(2)$ Å^3, $Z = 4$, and $D_{calc} = 1.535$ g/cm^3. The structure was refined to $R = 0.029$ and $R_w = 0.038$ for 428 variables and 4043 observations. Complex 2 crystallizes in monoclinic space group Cc with $a = 9.5782(8)$ Å, $b = 39.313(5)$ Å, $c = 11.252(2)$ Å, $V = 3911(4)$ Å^3, $Z = 4$, and $D_{calc} = 1.560$ g/cm^3. The structure was refined to $R = 0.027$ and $R_w = 0.034$ for 425 variables and 2301 observations. The mechanism of formation of 2 by deprotonation of 1 is discussed.

Introduction

The reaction of unsaturated organic ligands bound to transition metals is central to the study of organometallic chemistry. Examples of diene protonation as well as hydride abstraction from cyclic dienes have been reported. For example, Lewis and co-workers reported that the protonation of dienes bound to cobalt, rhodium, and iridium produce σ,η^2-diene complexes.[1] This group also described hydride abstraction from dienes bound to d^8 metal centers to obtain diene ligands bound in an η^3-allyl, η^2-olefin fashion.[2] We now describe a 1,2-η^2,6-σ-cycloocta-1,4-dienyl iridium complex formed by the deprotonation of an η^4-1,5-cyclooctadiene ligand using a variety of bases as mild as aryloxides.

Experimental Section

General Procedures. All reactions and manipulations were carried out under nitrogen using standard Schlenk line and dry box techniques unless otherwise noted. Solvents were degassed and purified by distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, sodium for toluene, and CaH$_2$ for CH$_2$Cl$_2$ and hexanes). Triphos and Proton Sponge were purchased from Aldrich Chemical Co. The complex [Ir(η^4-1,5-cyclooctadiene)Cl]$_2$ was prepared by a published literature method.[3] The NaOR reactants were prepared from the corresponding ROH and NaH in THF and precipitated with hexanes. ^{1}H NMR spectra were recorded on Gemini 200, Varian XL-200, and QE-300 spectrometers with chemical shifts reported in ppm referenced to internal SiMe$_4$. ^{31}P{^{1}H} NMR spectra were recorded on QE-300 and Varian XL-200 spectrometers at 121.4 and 80.96 MHz, respectively, with chemical shifts reported in ppm referenced to external H$_3$PO$_4$. Plasma desorption mass spectroscopy (PDMS) spectra were measured on an Applied

Biosystems Bio-Ion 20R instrument. Targets were prepared by electrospraying a CH$_2$Cl$_2$ solution of the analyte onto an aluminum-coated mylar disk. The target was inserted into the spectrometer immediately after drying.

Synthesis of [Ir(triphos)(η^4-1,5-cyclooctadiene)][Cl] (1). [Ir(η^4-1,5-cyclooctadiene)Cl]$_2$ (0.15 g, 0.22 mmol) and triphos [(Ph$_2$PCH$_2$CH$_2$)$_2$PPh] (0.24 g, 0.45 mmol) were stirred in CH$_2$Cl$_2$ overnight. Hexanes were added to induce precipitation. The pale green solid was collected by filtration, washed with hexanes, and dried under vacuum. Yield = 0.27 g, 69%. ^{1}H NMR (CDCl$_3$): δ 1.88 (s, 8H), δ 2.25 (d, 4H), δ 2.92 (m, 2H), δ 3.15 (m, 2H), δ 3.38 (m, 2H), δ 3.60 (m, 2H), δ 6.88 (t, 4H), δ 7.10 (t, 4H), δ 7.30–7.55 (m, 17H). ^{31}P{^{1}H} NMR (CDCl$_3$): A$_2$B, δ(P$_A$) = 27.4, δ(P$_B$) = 65.1; ^2J(P$_A$P$_B$) = 7.8 Hz. PDMS: m/z 833.2, 835.2. Anal. Calcd for C$_{42}$H$_{47}$ClIrOP$_3$: C, 56.78; H, 5.33; Cl, 3.99. Found: C, 55.91; H, 5.14; Cl, 4.07.

X-ray Structure Determination of [Ir(triphos)(η^4-1,5-cyclooctadiene)][Cl] (1). Crystals of 1 suitable for X-ray diffraction were obtained by addition of hexanes to a concentrated methylene chloride solution of 1 in air. The complex crystallized with one molecule of water in the crystal lattice. Data were collected using a Enraf-Nonius CAD4 diffractometer, and the structure was solved by MULTAN–least squares–Fourier methods. The crystallographic data are summarized in Table I. The final atomic coordinates are given in Table II. An ORTEP drawing of 1 is presented in Figure 1. For clarity, only the first carbon of each phenyl ring is shown. Selected bond distances and angles for 1 are listed in Tables III and IV, respectively.

Synthesis of Ir(triphos)(1,2-η^2,6-σ-cycloocta-1,4-dienyl) (2). Complex 2 was prepared by stirring complex 1 overnight with base [KOH, NaOCH$_3$, NaOC$_6$H$_5$, NaOC$_6$H$_4$-p-CH$_3$, NaOC$_6$H$_4$-p-C(CH$_3$)$_3$, N(C$_2$H$_5$)$_3$, pyridine, Proton Sponge] in THF. Hexanes were added to induce precipitation. Typical yields were 50%. ^{1}H NMR (CD$_2$Cl$_2$): δ 1.89 (s, 6H), δ 2.04 (m, 2H), δ 2.28 (m, 2H), δ 2.32 (s, 2H), δ 2.76 (m, 2H), δ 2.99 (m, 2H), δ 4.35 (br, 1H), δ 5.71 (br, 2H), δ 6.42–7.9 (m, 25H). ^{31}P{^{1}H} NMR (C$_6$D$_6$): A$_2$B, δ(P$_A$) = 27.8, δ(P$_B$) = 65.5; ^2J(P$_A$P$_B$) = 8.3 Hz. PDMS: m/z 833.3, 835.2. Anal. Calcd for C$_{43}$H$_{46}$Cl$_2$IrP$_3$: C, 56.21; H, 5.05. Found: C, 52.79; H, 5.57.

X-ray Structure Determination of Ir(triphos)(1,2-η^2,6-σ-cycloocta-1,4-dienyl) (2). X-ray-quality crystals were formed by slow evaporation of a saturated methylene chloride solution of 2. The complex crystallized with one molecule of methylene chloride in the crystal lattice. Data were collected using a Enraf-

* Author to whom correspondence should be addressed.
† Author to whom correspondence pertaining to crystallographic studies should be addressed.
(1) Evans, J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* 1977, 510.
(2) Lewis, J.; Parkins, A. W. *J. Chem. Soc. (A)* 1969, 953.
(3) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* 1974, *15*, 18.

Table I. Summary of Crystallographic Data for Complexes 1 and 2

	complex 1	complex 2
formula	$IrClP_3OC_{42}H_{47}$	$IrCl_2P_3C_{43}H_{46}$
formula wt	888.42	918.87
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	Cc
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
a, Å	15.165(2)	9.5782(8)
b, Å	10.791(2)	39.313(5)
c, Å	23.488(2)	11.252(2)
β, deg	90.839(5)	112.60(9)
V, Å^3	3843(2)	3911(4)
Z	4	4
D_{calcd}, g cm^{-3}	1.535	1.560
temp, °C	20	20
$F(000)$	1784.0	1840.0
cryst size, mm	0.32 × 0.22 × 0.21	0.47 × 0.38 × 0.29
μ(Mo Kα), cm^{-1}	36.84	36.88
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
monochromator	graphite	graphite
programs used	Enraf-Nonius MolEN	Enraf-Nonius SPD
2θ range, deg	4.00–45.00	4.00–45.00
no. of unique total data	5339	2611
no. of unique obsd data ($I > 3.0\sigma(I)$)	4043	2301
R	0.029	0.027
R_w	0.038	0.034

Nonius CAD4 diffractometer, and the structure was solved by MULTAN–least squares–Fourier methods. The crystallographic data are summarized in Table I. The final atomic coordinates are given in Table V. An ORTEP drawing of 2 is presented in Figure 2. For clarity, only the first carbon of each phenyl ring is shown. Selected bond distances and angles for 2 are listed in Tables VI and VII, respectively.

Results and Discussion

Treatment of a CH_2Cl_2 solution of [Ir(η^4-1,5-cyclooctadiene)Cl]$_2$ with 2 equiv of triphos leads to [Ir(triphos)-(η^4-1,5-cyclooctadiene)][Cl] (1). The ^{1}H NMR spectrum of 1 in $CDCl_3$ shows a complex multiplet from δ 2.8 to δ 3.7 ppm that corresponds to the eight CH_2 protons of the triphos ligand. The eight methylene protons of the cyclooctadiene ligand appear as a singlet at δ 1.88 ppm. The four olefinic protons of the cyclooctadiene appears as two peaks centered at δ 2.25 ppm. The presence of two olefinic peaks can be explained by the structure (Figure 1). The two olefinic groups are inequivalent since complex 1 is a distorted trigonal bipyramid. One olefinic group is in the axial position trans to a phosphorus atom, and the other is in the equatorial plane with the two remaining phosphorus atoms. The ^{31}P{^{1}H} NMR spectrum of 1 is an A_2B spin system (δ(P$_A$) = 27.4 ppm, δ(P$_B$) = 65.1 ppm) with coupling constant ^2J(P$_A$P$_B$) = 7.8 Hz. The PDMS spectrum of 1 shows parent peaks at m/z 833.2 and 835.2 in an approximate 1:2 ratio corresponding to the natural abundance of 37.3% Ir^{191} and 62.7% Ir^{193}. Elemental analytical data are consistently low in carbon and hydrogen for crystalline spectroscopically (^{1}H NMR, ^{31}P NMR, PDMS) pure samples that were dried overnight under vacuum.

In the presence of base [KOH, NaOCH$_3$, NaOC$_6$H$_5$, NaOC$_6$H$_4$-p-CH$_3$, NaOC$_6$H$_4$-p-C(CH$_3$)$_3$, N(C$_2$H$_5$)$_3$, pyridine, Proton Sponge] the η^4-1,5-cyclooctadiene ligand of 1 is deprotonated, yielding a 1,2-η^2,6-σ-cyclooctadiene-1,4-dienyl complex, 2. The ^{1}H NMR spectrum of 2 in CD_2Cl_2 shows a quartet of multiplets from δ 1.75 to δ 3.15 ppm

corresponding to the eight CH_2 protons of the triphos ligand. The six alkyl protons of the cyclooctadienyl ligand appear at δ 1.89 ppm at room temperature. The two olefinic protons of the coordinated double bond appear at δ 2.32 ppm. A broad peak at δ 4.35 ppm corresponds to the proton on the carbon that is σ-bonded to the iridium. The two olefinic protons of the uncoordinated double bond appear as a broad peak at δ 5.72 ppm. The ^{31}P{^{1}H} NMR spectrum of 2 is also an A_2B spin system (δ(P$_A$) = 27.8 ppm, δ(P$_B$) = 65.5 ppm) with coupling constant ^2J(P$_A$P$_B$) = 8.3 Hz. Compound 2 adopts a distorted trigonal bipyramidal geometry about the iridium, allowing the two diphenylethylphosphine arms of the triphos ligand to remain equivalent (Figure 2). The PDMS spectrum of 2 also shows parent peaks at m/z 833.3 and 835.2 in an approximate 1:2 ratio corresponding to the natural abundance of 37.3% Ir^{191} and 62.7% Ir^{193}. These are the same as the parent ion signals observed for 1 since protonation is a viable ionization mechanism in plasma desorption mass spectroscopy. In the PDMS spectrometer, 1 and 2 display equivalent signals due to protonation of 2. Elemental analytical data are consistently low in carbon even for crystalline spectroscopically (^{1}H NMR, ^{31}P NMR, PDMS) pure samples that were dried overnight under vacuum.

The σ-cyclooctadienyl coordination of complex 2 is similar to that of [(N(CH$_2$CH$_2$PPh$_2$)$_3$)IrH(1-σ-cycloocta-1,5-dienyl)][BPh$_4$], which was prepared by Bianchini and co-workers in 1986.[4] Their 1-σ-cycloocta-1,5-dienyl ligand was formed by the oxidative addition of one C–H bond of 1,5-cyclooctadiene. The tetradentate phosphorus–nitrogen ligand does not allow the additional η^2–π interaction of the cyclooctadienyl ligand. Significantly, in their reactions, there was no added base to cause deprotonation. Complex 1 does not show evidence for oxidative addition of its cyclooctadiene C–H bond.[5]

An important question pertaining to the formation of 2, then, is the role of the added base. We have considered two possible mechanisms for the formation of complex 2, shown in Schemes I and II.

The mechanism in Scheme I involves a Michael type addition of the base to the coordinated double bond of the cyclooctadiene ligand, followed by the elimination of the conjugate acid to give compound 2. The intermediates, Ia and Ib, are 18-electron complexes which could exist as two different structural isomers caused by a facial or meridonal arrangement of the triphos ligand. Attack at either end of the double bond of complex I would be expected to give different stereoisomers of the same 1,2-η^2,6-σ-cycloocta-1,4-dienyl complex. This mechanism is shown in pathways a and b of Scheme I.

The method of deprotonation by base in this pathway has precedence in that Calligaris and co-workers see nucleophilic attack of methoxide on a 1,5-cyclooctadiene ligand coordinated to iridium.[6] To test this hypothesis, we reacted NaOMe with 1 to see if the methoxide Michael type adduct could be isolated. Two structural isomers of an apparent methoxide Michael type adduct, 4 and 5, can be seen in the ^{31}P{^{1}H} NMR spectrum taken while following the reaction in THF/C$_6$D$_6$. The ^{31}P{^{1}H} NMR spectrum

(4) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Sabat, M.; Zanobini, F. *Organometallics* **1986**, *5*, 2557.

(5) [Ir(triphos)(η^4-1,5-cyclooctadiene)][Cl] was stirred overnight in chloroform. No evidence was seen for the formation of methylene chloride by ^{1}H NMR, and no change was seen in the ^{31}P{^{1}H} NMR spectrum.

(6) Bresciani-Pahor, N.; Calligaris, M.; Nardin, G.; Delise, P. *J. Chem. Soc., Dalton Trans.* **1976**, 762.

Table II. Positional Parameters and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of Complex 1[a]

atom	x	y	z	B (Å²)	atom	x	y	z	B (Å²)
Ir	0.20009(2)	0.01469(3)	0.19086(1)	2.076(6)	C(123)	0.1590(8)	−0.4797(9)	0.1006(5)	4.7(2)
P(1)	0.2150(1)	−0.1075(2)	0.10958(9)	2.40(4)	C(124)	0.0733(7)	−0.4806(9)	0.0797(5)	4.8(2)
P(2)	0.3392(1)	0.0778(2)	0.16591(9)	2.40(4)	C(125)	0.0298(7)	−0.372(1)	0.0678(4)	4.8(2)
P(3)	0.2758(1)	−0.0995(2)	0.26089(9)	2.35(4)	C(126)	0.0728(6)	−0.2561(9)	0.0758(4)	3.9(2)
C(1)	0.0560(5)	−0.0320(9)	0.1833(4)	3.2(2)	C(211)	0.3629(5)	0.2356(8)	0.1439(4)	2.7(2)
C(2)	0.0775(5)	−0.0282(8)	0.2410(4)	3.1(2)	C(212)	0.3834(6)	0.3265(8)	0.1854(4)	3.5(2)
C(3)	0.0491(6)	0.080(1)	0.2805(4)	4.4(2)	C(213)	0.4068(6)	0.4471(9)	0.1677(5)	4.0(2)
C(4)	0.1185(7)	0.185(1)	0.2846(4)	4.3(2)	C(214)	0.4094(7)	0.4768(9)	0.1109(5)	4.7(2)
C(5)	0.1783(6)	0.1886(8)	0.2338(4)	3.8(2)	C(215)	0.3856(8)	0.388(1)	0.0707(5)	5.0(3)
C(6)	0.1450(6)	0.1969(8)	0.1749(4)	3.6(2)	C(216)	0.3632(7)	0.2686(9)	0.0859(4)	3.9(2)
C(7)	0.0458(6)	0.199(1)	0.1624(5)	4.7(2)	C(311)	0.2711(6)	−0.2665(8)	0.2694(3)	2.9(2)
C(8)	0.0070(6)	0.070(1)	0.1518(4)	4.4(2)	C(312)	0.2022(6)	−0.3371(8)	0.2462(4)	3.3(2)
C(B1)	0.3336(5)	−0.1447(8)	0.1040(4)	3.1(2)	C(313)	0.1992(7)	−0.4648(9)	0.2566(4)	4.2(2)
C(B2)	0.3825(5)	−0.0197(8)	0.1074(4)	3.1(2)	C(314)	0.2635(7)	−0.5212(9)	0.2908(4)	4.0(2)
C(B3)	0.4153(5)	0.0532(8)	0.2263(3)	2.9(2)	C(315)	0.3304(7)	−0.4514(9)	0.3146(4)	4.2(2)
C(B4)	0.3954(5)	−0.0735(8)	0.2532(3)	2.7(2)	C(316)	0.3354(6)	−0.3249(9)	0.3040(4)	4.0(2)
C(111)	0.1928(6)	−0.0331(8)	0.0403(4)	2.9(2)	C(321)	0.2528(5)	−0.0548(8)	0.3344(3)	2.8(2)
C(112)	0.1685(6)	0.0899(9)	0.0383(4)	3.8(2)	C(322)	0.1896(6)	−0.1187(9)	0.3658(4)	3.4(2)
C(113)	0.1577(8)	0.147(1)	−0.0161(5)	5.4(3)	C(323)	0.1740(7)	−0.083(1)	0.4224(4)	4.3(2)
C(114)	0.1709(8)	0.081(1)	−0.0654(4)	5.8(3)	C(324)	0.2200(8)	0.014(1)	0.4461(4)	5.3(3)
C(115)	0.1961(8)	−0.045(1)	−0.0618(4)	5.3(3)	C(325)	0.2811(8)	0.078(1)	0.4156(4)	5.2(3)
C(116)	0.2071(7)	−0.1005(9)	−0.0095(4)	4.0(2)	C(326)	0.2990(7)	0.0429(9)	0.3596(4)	4.3(2)
C(121)	0.1594(6)	−0.2562(8)	0.0980(3)	2.8(2)	Cl	0.4571(2)	0.2290(2)	0.8411(1)	4.75(6)
C(122)	0.2030(6)	−0.3657(8)	0.1101(4)	3.6(2)	O(1000)	0.419(1)	0.123(1)	0.9623(6)	13.6(4)*

a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as follows: $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.
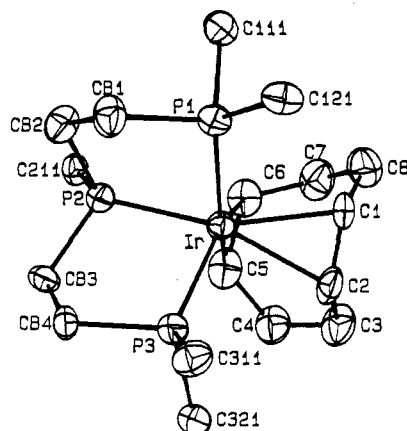

Figure 1. ORTEP drawing of [Ir(triphos)(η⁴-1,5-cyclooctadiene)][Cl] (1).

Table III. Selected Bond Lengths in Å for Complex 1

Ir–P(1)	2.334(2)	Ir–C(5)	2.158(7)
Ir–P(2)	2.301(2)	Ir–C(6)	2.166(7)
Ir–P(3)	2.342(2)	C(1)–C(2)	1.39(1)
Ir–C(1)	2.247(6)	C(5)–C(6)	1.47(1)
Ir–C(2)	2.263(7)		

Table IV. Selected Bond Angles in deg for Complex 1

P(1)–Ir–P(2)	81.88(6)	P(2)–Ir–C(6)	92.3(2)
P(1)–Ir–P(3)	103.01(6)	P(3)–Ir–C(1)	113.8(2)
P(2)–Ir–P(3)	86.86(6)	P(3)–Ir–C(2)	85.7(2)
P(1)–Ir–C(1)	85.1(2)	P(3)–Ir–C(5)	101.9(2)
P(1)–Ir–C(2)	113.6(2)	P(3)–Ir–C(6)	141.5(2)
P(1)–Ir–C(5)	153.0(2)	C(1)–Ir–C(5)	94.4(3)
P(1)–Ir–C(6)	114.4(2)	C(1)–Ir–C(6)	79.5(3)
P(2)–Ir–C(1)	160.1(2)	C(2)–Ir–C(5)	78.6(3)
P(2)–Ir–C(2)	163.0(2)	C(2)–Ir–C(6)	87.6(3)
P(2)–Ir–C(5)	90.5(2)		

of 4 in C₆D₆ shows an ABC spin system (δ(P$_A$) = 25.5 ppm, δ(P$_B$) = 60.0 ppm, δ(P$_C$) = 21.5 ppm) with coupling constants ^2J(P$_A$P$_B$) = 4.7 Hz, ^2J(P$_A$P$_C$) = 94 Hz, and ^2J(P$_B$P$_C$) < 2 Hz. These phosphorus coupling constants indicate that P$_A$ and P$_C$ are separated by a relatively wide angle. The location of these two phosphorus atoms in the equatorial plane of a trigonal bipyramidal structure would

be consistent with the 94-Hz coupling constant. The P$_A$P$_B$ and P$_B$P$_C$ coupling constants are relatively small, indicating the angles separating these atoms are closer to 90°. The phenyldiethylphosphine arm, P$_B$, of the triphos thus must be located in an axial position, suggesting this is the facial triphos isomer. The ^{31}P{^{1}H} NMR spectrum of 5 in C₆D₆ also shows an ABC spin system (δ(P$_A$) = 23.2 ppm, δ(P$_B$) = 54.9 ppm, δ(P$_C$) = 23.1 ppm) with coupling constants ^2J(P$_A$P$_B$) = ^2J(P$_B$P$_C$) = 3.5 Hz. These phosphorus coupling constants are relatively small, indicating an angle near 90° separating P$_A$P$_B$ and P$_B$P$_C$. These data suggest that 5 is the meridonal triphos isomer, where the two diphenylethylphosphine arms are in the axial positions and the phenyldiethylphosphine arm is in the equatorial plane with the methoxycyclooctenyl ligand. Refluxing the mixture of 4 and 5 in the absence of base in toluene for several hours yielded 2. Scheme III shows the facial and meridional structural isomers of Ir(triphos)(1,2-η²,6-σ-5-methoxycyclooctenyl).

When the reaction of 1 and NaOPh was followed by ^{31}P{^{1}H} NMR, an intermediate, 6, was observed as an ABC spin system (δ(P$_A$) = 23.3 ppm, δ(P$_B$) = 54.9 ppm, δ(P$_C$) = 23.2 ppm) with coupling constants ^2J(P$_A$P$_B$) = ^2J(P$_B$P$_C$) = 3.4 Hz. This is very similar to the meridonal triphos isomer of the methoxide adduct, 5, and is proposed as the meridonal triphos isomer of the phenoxide Michael type adduct of 1. In Scheme III the equilibrium appears to lie essentially completely toward species 6. None of the corresponding facial triphos isomer was seen in the ^{31}P-{^{1}H} NMR. This is a likely consequence of the sterics imposed by the phenoxy Michael type adduct in the equatorial position with two phosphorus atoms. Complex 6 converts to 2 over 48 h at room temperature.

We conclude that the Michael type addition mechanism in Scheme I best describes the way that weaker bases achieve the deprotonation of the 1,5-cyclooctadiene ligand. This mechanism is consistent with the ability to observe reaction intermediates when 1 reacts with weak bases, NaOCH₃, NaOC₆H₅, NaOC₆H₄-p-CH₃, and NaOC₆H₄-p-C(CH₃)₃. The Michael type adducts are intermediates

Table V. Positional Parameters and Their Estimated Standard Deviations for the Non-Hydrogen Atoms of Complex 2[a]

atom	x	y	z	B (Å^2)	atom	x	y	z	B (Å^2)
Ir	0.02480	0.36595(1)	0.96770	2.448(6)	C(124)	0.169(2)	0.3937(5)	1.537(1)	7.5(4)
P(1)	−0.0427(3)	0.40302(8)	1.0954(3)	3.20(6)	C(125)	0.026(3)	0.3830(3)	1.475(2)	7.2(3)
P(2)	−0.2269(3)	0.36687(8)	0.8423(3)	3.37(7)	C(126)	−0.044(1)	0.3852(4)	1.341(1)	5.7(3)
P(3)	−0.0247(3)	0.31416(7)	1.0363(3)	3.06(6)	C(211)	−0.298(1)	0.3781(3)	0.671(1)	4.0(3)
C(1)	−0.248(1)	0.3995(4)	1.049(1)	4.8(3)	C(212)	−0.381(2)	0.3552(4)	0.572(1)	6.0(4)
C(2)	−0.325(1)	0.3966(4)	0.903(1)	5.2(4)	C(213)	−0.433(3)	0.3663(5)	0.445(1)	8.6(6)
C(3)	−0.313(1)	0.3254(3)	0.848(1)	4.7(3)	C(214)	−0.402(2)	0.3985(5)	0.415(1)	7.4(5)
C(4)	−0.233(1)	0.3085(3)	0.976(1)	4.9(3)	C(215)	−0.326(2)	0.4205(4)	0.508(1)	6.4(4)
C(41)	0.111(1)	0.3922(2)	0.8391(8)	2.3(2)	C(216)	−0.274(2)	0.4106(4)	0.638(1)	5.5(4)
C(42)	0.105(1)	0.3542(3)	0.816(1)	3.9(3)	C(311)	0.034(2)	0.2769(2)	0.970(2)	3.5(2)
C(43)	0.235(1)	0.3313(4)	0.834(1)	4.7(3)	C(312)	0.141(2)	0.2543(4)	1.047(1)	4.9(4)
C(44)	0.354(1)	0.3271(4)	0.965(1)	5.4(3)	C(313)	0.191(2)	0.2274(4)	0.990(2)	6.6(4)
C(45)	0.355(1)	0.3399(3)	1.077(1)	3.9(3)	C(314)	0.131(2)	0.2225(4)	0.863(1)	5.9(4)
C(46)	0.260(1)	0.3689(3)	1.091(1)	3.4(2)	C(315)	0.025(2)	0.2436(4)	0.786(1)	6.5(4)
C(47)	0.325(2)	0.4024(4)	1.053(1)	4.9(3)	C(316)	−0.023(2)	0.2710(4)	0.837(1)	5.3(4)
C(48)	0.263(1)	0.4069(4)	0.906(1)	4.8(3)	C(321)	0.032(1)	0.3019(3)	1.206(1)	3.7(3)
C(111)	−0.030(1)	0.4489(3)	1.079(1)	3.5(3)	C(322)	0.156(2)	0.3154(4)	1.296(1)	5.5(4)
C(112)	0.019(2)	0.4622(3)	0.988(1)	4.0(3)	C(323)	0.204(2)	0.3069(4)	1.427(1)	6.6(5)
C(113)	0.043(2)	0.4966(3)	0.983(2)	5.3(3)	C(324)	0.124(2)	0.2840(4)	1.462(1)	7.2(4)
C(114)	−0.008(2)	0.5183(4)	1.054(2)	6.8(5)	C(325)	−0.002(2)	0.2697(4)	1.372(2)	7.1(4)
C(115)	−0.060(2)	0.5067(4)	1.141(1)	6.6(4)	C(326)	−0.044(2)	0.2772(4)	1.247(1)	5.9(4)
C(116)	−0.070(2)	0.4715(4)	1.155(1)	5.8(4)	Cl(1001)	0.598(2)	0.4998(5)	0.246(2)	29.8(7)*
C(121)	0.033(1)	0.3998(3)	1.270(1)	4.0(3)	Cl(1002)	0.393(2)	0.4972(5)	0.344(2)	29.3(7)*
C(122)	0.179(2)	0.4119(3)	1.339(1)	5.0(3)	C(1000)	0.428(4)	0.518(1)	0.226(4)	18(1)*
C(123)	0.250(2)	0.4091(4)	1.473(1)	6.4(4)					

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as follows: $(^4/_3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

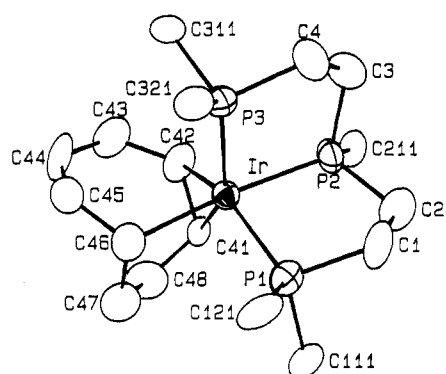**Figure 2.** ORTEP drawing of Ir(triphos)(1,2-η^2,σ-6-cycloocta-1,4-dienyl) (2).

**Table VI. Selected Bond Lengths in Å for Complex 2**

Ir–P(1)	2.306(5)	Ir–C(42)	2.18(1)
Ir–P(2)	2.279(7)	Ir–C(46)	2.15(3)
Ir–P(3)	2.291(3)	C(41)–C(42)	1.51(2)
Ir–C(41)	2.18(1)	C(44)–C(45)	1.35(2)

Table VII. Selected Bond Angles in deg for Complex 2

P(1)–Ir–P(2)	83.8(2)	P(1)–Ir–P(3)	102.0(1)
P(2)–Ir–P(3)	85.2(2)	P(1)–Ir–C(46)	92.3(7)
P(1)–Ir–C(41)	112.5(4)	P(1)–Ir–C(42)	153.1(4)
P(2)–Ir–C(41)	99.3(5)	P(2)–Ir–C(42)	97.3(4)
P(2)–Ir–C(46)	175.6(6)	P(3)–Ir–C(41)	145.5(3)
P(3)–Ir–C(42)	104.9(4)	P(3)–Ir–C(46)	97.7(5)
Ir–C(46)–C(45)	115(1)	Ir–C(46)–C(47)	107(1)
C(41)–Ir–C(46)	80.2(8)	C(42)–Ir–C(46)	85.2(8)

that cannot be isolated and spectroscopically characterized individually; therefore, $^{31}P\{^1H\}$ NMR analysis of reaction mixtures has been used for the characterization of these intermediates.

The mechanism in Scheme II involves the direct deprotonation by strong base of an alkyl C–H bond on the cyclooctadiene ligand, resulting in an allylic fragment. The allylic intermediate has precedence in the η^3-allyl coordination of hydride-abstracted cyclooctadiene seen by Lewis and co-workers.[2] The role of η^3-allyl intermediates is also well recognized in the isomerization of double bonds

Scheme I [a]
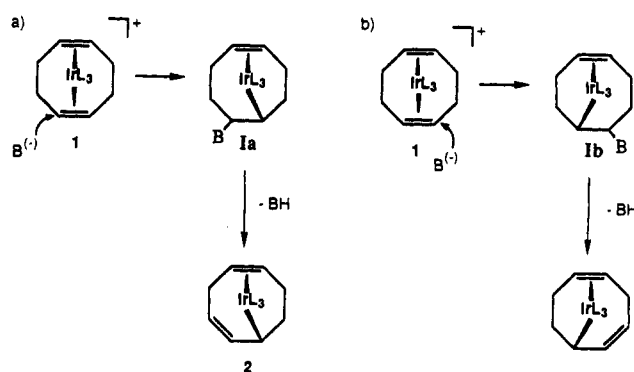
[a] L_3 = (PPh$_2$CH$_2$CH$_2$)$_2$PPh; B = KOH, NaOCH$_3$, NaOC$_6$H$_5$, NaOC$_6$H$_4$-p-CH$_3$, NaOC$_6$H$_4$-p-C(CH$_3$)$_3$, N(C$_2$H$_5$)$_3$, pyridine, Proton Sponge.

Scheme II [a]
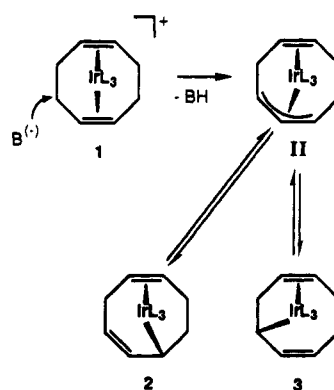
[a] L_3 = (PPh$_2$CH$_2$CH$_2$)$_2$PPh; B = KOH, NaOCH$_3$, NaOC$_6$H$_5$, NaOC$_6$H$_4$-p-CH$_3$, NaOC$_6$H$_4$-p-C(CH$_3$)$_3$, N(C$_2$H$_5$)$_3$, pyridine, Proton Sponge.

by iridium phosphine complexes.[7] The η^3-allyl fragment donates three electrons to the iridium, and therefore, either one of the triphos phosphorus atoms or, alternately, the olefinic part of the cyclooctadienyl ligand might be expected to dissociate. More likely, the allylic part of the

Scheme III

1   **4 (R = Me)**   **2**

5 (R = Me)

6 (R = C$_6$H$_5$, C$_6$H$_4$-*p*-CH$_3$, C$_6$H$_4$-*p*-C(CH$_3$)$_3$)
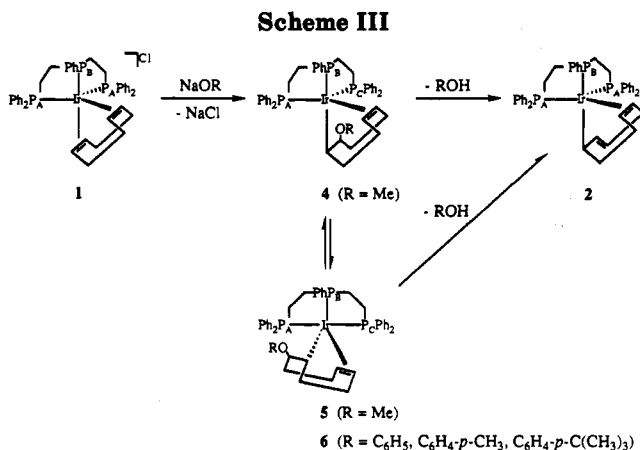
ring adopts an η^1-σ-allyl mode in order for the complex to retain an 18-electron configuration. Note that the symmetric η^3-allyl fragment can relax to either of the two σ-forms, corresponding to the 1,2-η^2,6-σ-cycloocta-1,4-dienyl (**2**) and the 1,2-η^2,4-σ-cycloocta-1,5-dienyl (**3**) complexes. Although our X-ray diffraction study revealed only the 1,4-dienyl isomer (**2**), the possibility that it and the corresponding 1,5-dienyl isomer (**3**) interconverted on the NMR time scale could not be excluded. Variable-temperature ^{31}P{^{1}H} NMR (CD$_3$C$_6$D$_5$) of **2** from 30 to −78 °C however does not show any coalescence. If exchange between **2** and **3** (Scheme II) is occurring, it is so facile that it cannot be frozen out. More likely, **2** is significantly more stable than **3** on account of the unfavorble sterics in the 1,2-η^2,4-σ-cycloocta-1,5-dienyl structure.

In the reactions of **1** with KOH, N(C$_2$H$_5$)$_3$, pyridine, and Proton Sponge, the only species observed were **1** and **2**. This supports the direct deprotonation mechanism in Scheme II since the 20-electron η^3-allyl intermediate, **II**,

would be expected to collapse to the σ-allyl very fast. The non-Michael type pathway in Scheme II is apparently followed when a variety of strong bases are employed to achieve the transformation of **1** to **2**. These stronger bases, KOH, N(C$_2$H$_5$)$_3$, pyridine, and Proton Sponge, caused the formation of **2** to occur much more quickly than the weaker aryloxide and alkoxide bases. We note that Proton Sponge achieved the transformation of **1** to **2**, yet would have enormous steric difficulty achieving formation of a Michael type adduct.

Conclusion

The mechanism that best describes our results when the bases NaOCH$_3$, NaOC$_6$H$_5$, NaOC$_6$H$_4$-*p*-CH$_3$, or NaOC$_6$H$_4$-*p*-C(CH$_3$)$_3$ are used to prepare **2** is the Michael type addition followed by alcohol or phenol elimination pathway shown in Scheme I. When the base is KOH, N(C$_2$H$_5$)$_3$, pyridine, or proton sponge, the mechanism of deprotonation that best describes our results is the direct deprotonation shown in Scheme II. The weaker aryloxide and alkoxide bases must be unable to achieve the direct deprotonation, so they react instead through the Michael type adduct with subsquent elimination. Stronger bases are able to deprotonate **1** directly.

OM920725E

(7) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* 1978, 694.