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Synthesis and Reactivity of Alkoxy(η^4-cycloocta-1,5-diene)iridium(I) and -rhodium(I) M(OR)(cod)(PCy$_3$) Compounds. X-ray Crystal Structure of the Alkynyl Ir(C≡CPh)(cod)(PCy$_3$) Complex

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The synthesis and reactivity of the alkoxy(η^4-cycloocta-1,5-diene)iridium(I) Ir(OR)(cod)(PCy$_3$) (R = Me, Et, or Ph; Cy = cyclohexyl; cod = cycloocta-1,5-diene) complexes are described. They are prepared by reaction of $[Ir(\mu\text{-}OR)(cod)]_2$ with PCy$_3$. The synthesis of Rh(OPh)(cod)(PCy$_3$) by reaction of $[Rh(\mu\text{-}OMe)(cod)]_2$ with PCy$_3$ and PhOH is also reported. Treatment of $[Ir(\mu\text{-}OMe)(cod)]_2$ with PCy$_3$ in methanol for 24 h gives a mixture of the hydrido $IrH_5(PCy_3)_2$ and *mer*-$IrH_3(CO)(PCy_3)_2$ complexes. Ir(OEt)(cod)(PCy$_3$) reacts with HSiR$_3$ (SiR$_3$ = SiEt$_3$ or SiMe$_2$Ph) leading to the formation of $IrH_2(SiR_3)(cod)(PCy_3)$. Ir(OR)(cod)(PCy$_3$) undergoes alkoxy exchange with phenol. Alkoxy exchange is also observed in the reaction of Ir(OEt)(cod)(PCy$_3$) with phenylacetylene (HC≡CPh); the resulting Ir(C≡CPh)(cod)(PCy$_3$) complex has been characterized by X-ray diffraction. Ir(C≡CPh)(cod)(PCy$_3$): triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.3726$ (6) Å, $b = 11.1529$ (4) Å, $c = 12.4738$ (5) Å, $\alpha = 105.307$ (4)°, $\beta = 101.845$ (3)°, and $\gamma = 107.607$ (4)°. The structure was solved by Patterson and difference direct methods and refined to a conventional agreement factor of 0.034. The coordination around iridium is slightly distorted square planar, with a Ir—C(1) distance of 1.998 (6) Å and a C(1)—C(2) (C≡C) bond length and C(1)—C(2)—C(3) angle of 1.200 (10) Å and 176.5 (8)°, respectively.

Introduction

Considerable interest has recently been focused on the chemistry of alkoxide complexes of the group 8–10 metals. Although alkoxides of these late transition metals may participate in several important catalytic reactions,[1] few compounds of this type are known.[2] The difficulty in isolating such metal alkoxides is mostly due to their relatively easy decomposition by β-hydride elimination[3] or hydrolysis.[4] Our recent work on the catalytic activity of systems derived from the reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ (cod = cycloocta-1,5-diene) with group 15 atom donor ligands (L), in hydrosilylation[5] and hydrogen-transfer reactions[6], have resulted in the isolation of the $IrH(cod)L_2$[6] and $IrH_2(SiR_3)(cod)L_2$[7] complexes. We felt that terminal alkoxide species may participate in the formation of those complexes, and we thus began our study with the expectation of isolating alkoxide compounds from the reaction of $[M(\mu\text{-}OR)(cod)]_2$ (M = Ir or Rh) with PCy$_3$. Here, we wish to report the synthesis and reactivity of complexes of the type M(OR)(cod)(PCy$_3$) (M = Ir or Rh).

Results and Discussion

Preparation. The reaction of PCy$_3$ with $[Ir(\mu\text{-}OMe)(cod)]_2$ in methanol for 30 min leads to the orange, air-stable, Ir(OMe)(cod)(PCy$_3$) complex (eq 1). When the

$$\tfrac{1}{2}[Ir(\mu\text{-}OMe)(cod)]_2 + PCy_3 \xrightarrow{\text{MeOH, 30 min}} Ir(OMe)(cod)(PCy_3) \quad (1)$$

reaction is allowed to proceed for a longer time, a more complex reaction occurs (see reactivity). Formulation of the complex is supported by its microanalyses and its ^1H NMR and IR spectra. The ^1H NMR spectrum is compatible with a square-planar structure, analogous to that of IrCl(cod)(PCy$_3$).[8] It shows a singlet at 3.44 ppm due to the methoxy protons, two broad signals at 4.34 and 2.78 ppm attributable to the vinyl protons of the cod trans to PCy$_3$ and OCH$_3$, respectively, and complex aliphatic resonances (1.1–2.3 ppm) of the PCy$_3$ and cod ligands. The presence of the methoxy group is also supported by the IR spectrum, which shows a band at 1072 cm^{-1} assignable to ν(C–O).

The Ir(OMe)(cod)(PCy$_3$) complex is the only product initially formed in the reaction of $[Ir(\mu\text{-}OMe)(cod)]_2$ with PCy$_3$, as is deduced by its ^1H NMR spectrum. The ^1H NMR spectrum of a mixture of $[Ir(\mu\text{-}OMe)(cod)]_2$ and PCy$_3$, in a 1:1 ratio of Ir to PCy$_3$, in CDCl$_3$ shows only the resonances due to Ir(OMe)(cod)(PCy$_3$). Upon addition of

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a second mole of PCy$_3$ the spectrum remains unchanged. In contrast, the reaction of the iridium dimer with PPh$_3$ suggested the formation of an equilibrium between a species containing 1 and 2 mol of PPh$_3$ per iridium (eq 2).[7b]

$$\mathrm{Ir(OMe)(cod)(PPh_3)} \overset{\mathrm{PPh_3}}{\rightleftharpoons} \mathrm{Ir(OMe)(cod)(PPh_3)_2} \quad (2)$$

The different behavior of PCy$_3$ and PPh$_3$ in this reaction is most probably due to a steric effect; the more sterically demanding PCy$_3$ ligand disfavors the formation of a pentacoordinated species, similar to that found with IrCl(cod)(PCy$_3$).[8]

The analogous Ir(OR)(cod)(PCy$_3$) (R = Et or Ph) compounds have been synthesized by reaction of PCy$_3$ with [Ir(μ-OEt)(cod)]$_2$ in ethanol or with [Ir(μ-OPh)(cod)]$_2$ in acetone. These complexes also can be prepared by treatment of [Ir(μ-OMe)(cod)]$_2$ with PCy$_3$ in ethanol or in a phenol–acetone mixture. By a similar procedure, Rh(OPh)(cod)(PCy$_3$) has been isolated from the reaction of [Rh(μ-OMe)(cod)]$_2$ with PCy$_3$ in phenol–acetone. Microanalysis and ^{1}H NMR and IR data of the abovementioned compounds are consistent with the proposed formulation. The ^{1}H NMR spectra show two signals corresponding to the inequivalent vinyl protons of the cod, in concordance with a square-planar geometry. In addition, the IR spectra show bands around 1100–1265 cm^{-1} attributable to ν(C–O).

It is of interest to note that the synthetic strategy used for the preparation of Ir(OR)(cod)(PCy$_3$), cleavage of the alkoxy bridge in [Ir(μ-OR)(cod)]$_2$ by a phosphine, provides a new procedure for the synthesis of terminal alkoxide complexes of iridium(I) and rhodium(I). Until now, the chemistry of terminal alkoxide iridium(I) and rhodium(I) compounds has been limited to complexes of the type *trans*-M(OR)(CO)(PR$_3$)$_2$ (M = Ir,[9] Rh[10]), Ir(OMe)(CO)(PPh$_3$)$_2$(TCME),[11] [AsPh$_4$][Rh(1,2-O$_2$C$_6$Cl$_4$)(CO)$_2$],[12] [AsPh$_4$][Rh(2,3-O$_2$C$_{10}$H$_6$)(CO)$_2$],[12] and [NBu$_4$][Rh(2,3-O$_2$C$_{10}$H$_6$)(cod)].[13]

Reactivity. When the reaction of [Ir(μ-OMe)(cod)]$_2$ with PCy$_3$, in an Ir to P ratio of 1:1 or 1:2, in methanol is allowed to proceed for 24 h at room temperature, a mixture of *mer*-IrH$_3$(CO)(PCy$_3$)$_2$ and IrH$_5$(PCy$_3$)$_2$ precipitates from the solution (eq 3). Formation of the known IrH$_5$(PCy$_3$)$_2$[14]

$$[\mathrm{Ir}(\mu\text{-OMe})(\mathrm{cod})]_2 + 2 \text{ or } 4\ \mathrm{PCy_3} \xrightarrow{\mathrm{MeOH,\ 24\ h}} \mathrm{IrH_5(PCy_3)_2} + mer\text{-}\mathrm{IrH_3(CO)(PCy_3)_2} \quad (3)$$

is deduced by the presence in the ^{1}H NMR spectrum of the precipitate in CDCl$_3$ of a triplet at −11.28 ppm ($^2J_{\mathrm{H-P}}$ = 12.1 Hz) and a band in the IR spectrum at 1940 cm^{-1} (ν(Ir–H)). Although we have not isolated *mer*-IrH$_3$(CO)(PCy$_3$)$_2$ in the pure state, the high-field ^{1}H NMR spectrum (−12.16 (td, $^2J_{\mathrm{H-P}}$ = 14.6 Hz, $^2J_{\mathrm{H-H}}$ = 4.4 Hz), −12.83 ppm (tt, $^2J_{\mathrm{H-P}}$ = 19.3 Hz, $^2J_{\mathrm{H-H}}$ = 4.4 Hz)) and the IR spectrum (2070, 2050, 1925, and 1788 cm^{-1}) support the proposed formulation, by comparison with the spectroscopic data reported for *mer*-IrH$_3$(CO)(PPh$_3$)$_2$.[15] In an experiment carried out by using an Ir to PCy$_3$ ratio of 1:2, after 24 h of reaction the composition of the precipitate was approximately 5% of IrH$_5$(PCy$_3$)$_2$ and 95% of IrH$_3$(CO)(PCy$_3$)$_2$, according to the integration of the high-field signals in the ^{1}H NMR spectrum; the remaining solution was analyzed by GC. The presence of cycloocta-1,5-diene (5%), cycloocta-1,3-diene (25%), and cyclooctene (70%) was demonstrated. The use of a 1:1 ratio of Ir to PCy$_3$ gives the same products along with unreacted dimer. It is worth noting that, as we have previously reported,[6] treatment of [Ir(μ-OMe)(cod)]$_2$ with 4 molar equiv of PPh$_3$ in methanol at room temperature for 3 h gives IrH(cod)(PPh$_3$)$_2$ (eq 4). The same complex, IrH(cod)(PPh$_3$)$_2$,

$$[\mathrm{Ir}(\mu\text{-OMe})(\mathrm{cod})]_2 + 4\mathrm{PPh_3} \xrightarrow{\mathrm{MeOH,\ 24\ h}} 2\mathrm{IrH(cod)(PPh_3)_2} \quad (4)$$

is also formed when this reaction is allowed to proceed for 24 hours. Formation of hydrido or hydrido carbonyl complexes by β-hydrogen elimination from alkoxy groups has numerous precedents.[16] Interestingly, although dehydrogenation of alcohols with long carbon chains usually is easier,[17] Ir(OEt)(cod)(PCy$_3$) remains unchanged when treated with PCy$_3$ in ethanol for 24 h.

The easy synthesis and stability of Ir(OEt)(cod)(PCy$_3$) allow us to study the reactivity of this type of complex toward silanes. Addition of 2 molar equiv of HSiR$_3$ (SiR$_3$ = SiEt$_3$, SiMe$_2$Ph) to Ir(OEt)(cod)(PCy$_3$) gives IrH$_2$(SiR$_3$)(cod)(PCy$_3$) and EtOSiR$_3$ (detected by GC–MS)[18] (eq 5). The reaction most probably involves oxidative

$$\mathrm{Ir(OEt)(cod)(PCy_3)} + 2\mathrm{HSiR_3} \rightarrow \mathrm{IrH_2(SiR_3)(cod)(PCy_3)} + \mathrm{EtOSiR_3} \quad (5)$$

addition of HSiR$_3$ to Ir(OEt)(cod)(PCy$_3$), followed by reductive elimination of EtOSiR$_3$ and subsequent oxidative addition of HSiR$_3$ to a hypothetical intermediate, IrH(cod)(PCy$_3$), as we have postulated for the formation of the related IrH$_2$(SiR$_3$)(cod)(PPh$_3$).[7] Unfortunately, as in the preparation of IrH$_2$(SiR$_3$)(cod)(PPh$_3$), we have been unable to detect the proposed hydrido intermediate. The new hydridosilyl complexes have been fully characterized by elemental analyses and IR and ^{1}H NMR spectroscopy.

Exchange of the alkoxy group has been observed on treatment with phenol. Thus, addition of 1 molar equiv of phenol to Ir(OR)(cod)(PCy$_3$) (R = Me, Et) results in the total conversion of the starting material (eq 6), according

$$\mathrm{Ir(OR)(cod)(PCy_3)} + \mathrm{PhOH} \rightarrow \mathrm{Ir(OPh)(cod)(PCy_3)} + \mathrm{ROH} \quad (6)$$

$$\mathrm{R = Me,\ Et}$$

to ^{1}H NMR measurements. Similarly, reaction of 1 molar equiv of phenylacetylene with Ir(OEt)(cod)(PCy$_3$) gives Ir(C≡CPh)(cod)(PCy$_3$). Microanalysis and IR and ^{1}H NMR data are consistent with the proposed formulation. To further characterize this terminal alkynyl compound, we have determined its crystal structure.

X-ray Crystal Structure of Ir(C≡CC$_6$H$_5$)(η^4-C$_8$H$_{12}$)(P(C$_6$H$_{11}$)$_3$). The coordination geometry around

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(18) MS: *m/Z* (relative intensity) EtOSiEt$_3$ 160 (M, 4), 131 (M − Et, 100); EtOSiMe$_2$Ph 180 (M, 19), 165 (M − Me, 100).

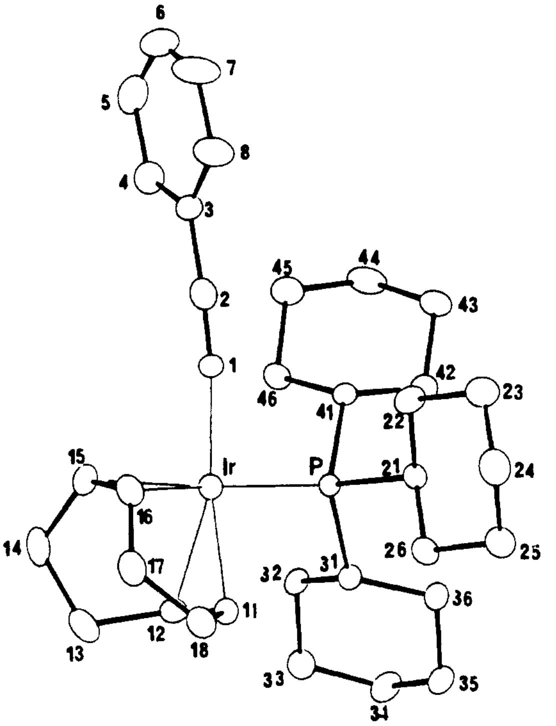

Figure 1. ORTEP drawing of the molecular structure of Ir($C{\equiv}CC_6H_5$)(η^4-C_8H_{12})($P(C_6H_{11})_3$).

the iridium is approximately square-planar (see Figure 1). The deviation of the iridium from the coordination plane (midpoints of the cycloocta-1,5-diene olefinic bonds, P atom, C atom of the $C{\equiv}CC_6H_5$) is 0.026 (1) Å. The Ir–C(1) length (1.998 (6) Å) (Table II) is consistent with a single bond from Ir(I) to a C(sp) atom and indicates a low degree of metal-to-ligand back-bonding.[19] The C(1)–C(2) bond length and C(1)–C(2)–C(3) angle are 1.200 (10) Å and 176.5 (8)°, respectively; a slight bending in the Ir–C–C moiety is present (Ir–C(1)–C(2) = 172.8 (6)°); similar values have been found for related complexes containing terminal alkynyl groups.[20] The C–C distances of the aromatic ring fall in the range 1.319 (35)–1.405 (23) Å; the shortest distances are those of C(5)–C(6) (1.361 (21) Å) and C(6)–C(7) (1.319 (35) Å) and correspond to the highest values of the thermal parameters. The different structural influence of the phenylacetylide group and the triphenylphosphine ligand is seen in the significant differences in Ir–C(olefin) distances (2.162 (7)–2.197 (8) Å). The cycloocta-1,5-diene presents a noncrystallographic approximate twofold axis (see Table II). The cyclohexane rings show chair conformations with torsion angular values ranging, in absolute values, between 52.4 (8) and 60.7 (6)°; the C–C distances range from 1.509 (10) to 1.550 (8) Å.

Table I. Crystal Data and Data Collection Parameters

	Crystal Data
formula	$C_{34}H_{50}IrP$
cryst habit	rectangular prism
cryst size, mm	0.03 × 0.08 × 0.28
symmetry	triclinic, $P\bar{1}$
unit cell determinatn	least-squares fit from 90 reflctns ($2 < \theta < 45°$)
unit cell dimens	12.3726 (6), 11.1529 (4), 12.4738 (5) Å 105.307 (4), 101.845 (3), 107.607 (4)°
packing: V, Å^3; Z	1504.4 (1); 2
D_{calcd}, g·cm^{-3}; M, $F(000)$	1.506; 682.0; 692
μ, cm^{-1}	90.69
	Experimental Data
technique	Philips diffractometer (PW 1100) bisecting geometry graphite-oriented monochromator, Cu Kα $\omega/2\theta$ scans; scan width 1.5 detector apertures 1.0 × 1.0°
total measurements	up to 65°
speed	1 min/reflctn
no. of reflctns	
measd	5097
independent	5097
obsd	4699 [$3\sigma(I)$ criterion]
std reflctns	2 reflctns every 90 min variation, no
max–min transmissn, factors	1.139–0.760
	Solution and Refinement
solution	Patterson function and DIRDIF
refinement	least squares on F_o with 2 blocks
parameters	
no. of variables	525
degrees of freedom	4174
ratio of freedom	9.0
H atoms	difference synthesis
final shift/error	0.16
max thermal value	$U_{11}[C(6)]$ = 0.23 (2) Å^2
final ΔF peaks	1.22 e·A^{-3} near Ir and P atoms
extincn correctn	no
final R and R_w	0.034 and 0.037
computer and programs	VAX 11/750 XRAY76 System[23] and DIRDIF[24]
scattering factors	ref 25

Table II. Selected Geometrical Parameters[a]

	(a) Bond Distances (Å)		
Ir–C(1)	1.998 (6)	C(11)–C(12)	1.395 (9)
Ir–P	2.341 (2)	C(15)–C(16)	1.409 (10)
Ir–C(11)	2.162 (7)	C(1)–C(2)	1.200 (10)
Ir–C(12)	2.172 (5)	C(2)–C(3)	1.447 (11)
Ir–C(15)	2.190 (8)	C(21)–P	1.857 (6)
Ir–C(16)	2.197 (8)	C(31)–P	1.854 (6)
		C(41)–P	1.854 (7)
	(b) Bond Angles (deg)		
C(1)–Ir–P	89.0 (2)	C(21)–P–C(31)	105.0 (3)
M(12)–Ir–P	96.6 (1)	C(21)–P–C(41)	101.2 (3)
M(12)–Ir–M(56)	85.0 (2)	C(31)–P–C(41)	108.7 (3)
M(56)–Ir–C(1)	89.4 (2)	Ir–C(1)–C(2)	172.8 (6)
C(1)–C(2)–C(3)	176.5 (8)		
	(c) Some Least-Squares Planes		
(i) Ir,M(12),M(56)		(ii) Ir,P,C,(1)	
	i∧ii 3.3 (2)°		

[a] M(12) and M(56) are the midpoints of the olefinic bonds in the COD.

Experimental Section

General Data. All reactions were carried out at room temperature under a nitrogen atmosphere by using standard Schlenk techniques. [Ir(μ-OR)(cod)]$_2$[21] (R = Me, Et, Ph) and [Rh(μ-OMe)(cod)]$_2$[22] were prepared as previously reported. ^{1}H NMR spectra were measured in $CDCl_3$ solution at room temperature on a Varian XL 200 spectrometer. IR spectra were recorded on

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Table III. Final Atomic Coordinates

atom	*x/a*	*y/b*	*z/c*
IR	0.21178 (2)	0.22680 (2)	0.46935 (2)
P	0.1800 (1)	0.3397 (1)	0.3395 (1)
C(1)	0.2041 (6)	0.0746 (6)	0.3364 (5)
C(2)	0.2107 (6)	−0.0163 (7)	0.2644 (6)
C(3)	0.2267 (7)	−0.1223 (7)	0.1812 (6)
C(4)	0.3391 (10)	−0.1068 (13)	0.1706 (8)
C(5)	0.3561 (16)	−0.2108 (19)	0.0924 (11)
C(6)	0.2613 (21)	−0.3260 (16)	0.0241 (10)
C(7)	0.1544 (19)	−0.3423 (10)	0.0347 (9)
C(8)	0.1331 (11)	−0.2417 (8)	0.1110 (7)
C(11)	0.1613 (6)	0.3502 (6)	0.5995 (5)
C(12)	0.2855 (5)	0.3955 (5)	0.6333 (5)
C(13)	0.3596 (6)	0.3723 (7)	0.7344 (6)
C(14)	0.3849 (6)	0.2452 (9)	0.6926 (6)
C(15)	0.2910 (6)	0.1383 (7)	0.5857 (6)
C(16)	0.1680 (6)	0.0964 (6)	0.5718 (6)
C(17)	0.1178 (5)	0.1479 (7)	0.6652 (6)
C(18)	0.0864 (5)	0.2676 (7)	0.6545 (6)
C(21)	0.0182 (5)	0.2888 (6)	0.2670 (5)
C(22)	−0.0433 (6)	0.1365 (6)	0.2001 (6)
C(23)	−0.1761 (6)	0.0960 (7)	0.1376 (7)
C(24)	−0.2403 (6)	0.1444 (8)	0.2200 (7)
C(25)	−0.1798 (5)	0.2938 (7)	0.2846 (6)
C(26)	−0.0484 (5)	0.3315 (7)	0.3511 (5)
C(31)	0.2374 (5)	0.5251 (5)	0.4077 (5)
C(32)	0.3755 (5)	0.5875 (6)	0.4450 (5)
C(33)	0.4242 (5)	0.7354 (6)	0.5220 (6)
C(34)	0.3690 (6)	0.8149 (6)	0.4635 (6)
C(35)	0.2332 (5)	0.7522 (6)	0.4221 (6)
C(36)	0.1858 (5)	0.6051 (6)	0.3431 (5)
C(41)	0.2331 (5)	0.2962 (5)	0.2114 (5)
C(42)	0.2106 (6)	0.3623 (7)	0.1212 (5)
C(43)	0.2324 (7)	0.2933 (7)	0.0100 (6)
C(44)	0.3605 (7)	0.2971 (8)	0.0355 (6)
C(45)	0.3899 (6)	0.2398 (8)	0.1308 (6)
C(46)	0.3644 (5)	0.3076 (6)	0.2422 (5)

a Perkin-Elmer 783 spectrophotometer. Elemental analyses were carried out with a Perkin-Elmer 240 C elemental analyzer.

Synthesis of the Complexes Ir(OMe)(cod)(PCy$_3$). [Ir(μ-OMe)(cod)]$_2$ (60 mg, 0.09 mmol) and PCy$_3$ (51 mg, 0.18 mmol) in methanol were stirred, at room temperature, for 30 min. The yellow precipitate was filtered, washed with methanol, and dried under vacuum: yield 62 mg (56%). Anal. Calcd for $C_{27}H_{48}IrOP$: C, 53.00; H, 7.90. Found: C, 52.65; H, 7.74. IR (Nujol): ν(C–O) 1072 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$ (cod)), 2.79 (br, 2 H, =CH (cod)), 3.44 (s, 3 H, OCH$_3$), 4.34 (br, 2 H, =CH (cod)).

Ir(OEt)(cod)(PCy$_3$). [Ir(μ-OEt)(cod)]$_2$ (400 mg, 0.58 mmol) was added to a solution of PCy$_3$ (325 mg, 1.16 mmol) in ethanol. After 3 h at room temperature the resulting yellow precipitate was filtered, washed with ethanol, and dried under vacuum: yield 587 mg (81%). The Ir(OEt)(cod)(PCy$_3$) complex also can be prepared by this method using [Ir(μ-OMe)(cod)]$_2$ as the starting material. Anal. Calcd for $C_{28}H_{50}IrOP$: C, 53.73; H, 8.05. Found: C, 53.69; H, 7.96. IR (Nujol): ν(C–O) 1110 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 1.06 (t, 2 H, J_{H-H} = 7 Hz, OCH$_2$), 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$ (cod)), 2.79 (br, 2 H, =CH (cod)), 3.93 (q, 3 H, J_{H-H} = 7 Hz, OCH$_2$CH$_3$), 4.57 (br, 2 H, =CH (cod)).

Ir(OPh)(cod)(PCy$_3$). [Ir(μ-OPh)(cod)]$_2$ (53 mg, 0.06 mmol) was added to a solution of PCy$_3$ (36 mg, 0.12 mmol) in diethyl ether, and the mixture was stirred at room temperature for 5 h. The solution was concentrated and addition of acetone caused the precipitation of a yellow solid. This was filtered, washed with acetone, and dried under vacuum: yield 44 mg (47%). The Ir(OPh)(cod)(PCy$_3$) complex also can be prepared by treatment of [Ir(μ-OMe)(cod)]$_2$ (80 mg, 0.12 mmol) with PCy$_3$ (68 mg, 0.24 mmol) in a solution of phenol (excess) in acetone. After 3 h at room temperature the yellow precipitate was filtered, washed with acetone, and dried under vacuum: yield 44 mg (41%). Anal. Calcd for $C_{32}H_{50}IrOP$: C, 57.03; H, 7.03. Found: C, 56.48; H, 7.26. IR (Nujol): ν(C–O) 1265 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$(cod)), 2.9 (br, 2 H, =CH (cod)), 4.48 (br, 2 H, =CH (cod)), 6.6 (d, J_{H-H} = 8 Hz, 3 H, C_6H_5), 7.9 (t, J_{H-H} = 8 Hz, 2 H, C_6H_5).

Rh(OPh)(cod)(PCy$_3$). A mixture of [Rh(μ-OMe)(cod)]$_2$ (100 mg, 0.2 mmol), PCy$_3$ (112 mg, 0.4 mmol), and phenol (excess) in acetone was stirred for 3 h. The resulting yellow precipitate was filtered, washed with acetone, and dried under vacuum: yield 150 mg (62%). Anal. Calcd for $C_{32}H_{50}OPRh$: C, 65.74; H, 8.60. Found: C, 65.29; H, 8.40. IR (Nujol): ν(C–O) 1245 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$ (cod)), 3.36 (br, 2 H, =CH (cod)); 4.78 (br, 2 H, =CH (cod)), 6.46 (t, J_{H-H} = 8 Hz, 1 H, C_6H_5); 6.6 (d, J_{H-H} = 8 Hz, 2 H, C_6H_5), 7.0 (t, J_{H-H} = 8 Hz, 2 H, C_6H_5).

Formation of IrH$_5$(PCy$_3$)$_2$ and *mer*-IrH$_3$(CO)(PCy$_3$)$_2$. A mixture of [Ir(μ-OMe)(cod))]$_2$ (70 mg, 0.1 mmol) and PCy$_3$ (118 mg, 0.4 mmol) in methanol was allowed to react at room temperature for 24 h. The white precipitate that formed was filtered, washed with methanol, and dried under vacuum: 105 mg of a white solid was obtained. IR (Nujol): ν(C≡O) and ν(Ir—H) 2070, 2050, 1940, 1925, 1788 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): −11.28 (t, J_{H-P} = 12.1 Hz, IrH), −12.16 (td, J_{H-P} = 14.6 Hz, J_{H-H} = 4.4 Hz, IrH), −12.83 (tt, J_{H-P} = 19.3 Hz, J_{H-H} = 4.4 Hz, IrH), 1.1–2.3 (m, C_6H_{11}).

IrH$_2$(SiEt$_3$)(cod)(PCy$_3$). A solution of Ir(OEt)(cod)(PCy$_3$) (100 mg, 0.16 mmol) in acetone was treated with HSiEt$_3$ (53 μL, 0.33 mmol), and the mixture was stirred for 30 min. The solution was concentrated under reduced pressure, and methanol was added to give a white precipitate that was filtered, washed with methanol, and dried under vacuum: yield 73 mg (66%). Anal. Calcd for $C_{32}H_{62}IrPSi$: C, 5.05; H, 8.95. Found: C, 55.14; H, 9.03. IR (Nujol): ν(Ir–H) 2120 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): −13.52 (d, 2 H, J_{H-P} = 21 Hz, IrH), 0.86 (br, 15 H, SiCH$_2$CH$_3$), 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$ (cod), 3.56 (br, 4 H, =CH (cod)).

IrH$_2$(SiMe$_2$Ph)(cod)(PCy$_3$). The complex was prepared by using the procedure described for IrH$_2$(SiEt$_3$)(cod)(PCy$_3$), with Ir(OEt)(cod)(PCy$_3$) (100 mg, 0.16 mmol) and HSiMe$_2$Ph (49 μL, 0.32 mmol). A white solid was obtained in 79 mg (69%) yield. Anal. Calcd for $C_{34}H_{58}IrPSi$: C, 56.87; H, 7.86. Found: C, 56.50; H, 7.51. IR (Nujol): ν(Ir–H) 2120 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): −13.30 (d, 2 H, J_{H-P} = 21 Hz, IrH), 0.72 (br, 6 H, SiCH$_3$), 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$ (cod)), 3.58 (br, 4 H, =CH (cod)), 7.11 (d, 1 H, J_{H-H} = 7 Hz, C_6H_5), 7.20 (t, 2 H, J_{H-H} = 7 Hz, C_6H_5), 7.58 (d, 2 H, J_{H-H} = 7 Hz, C_6H_5).

Exchange of the Alkoxy Group in Ir(OR)(cod)(PCy$_3$) with Phenol. The reactions were carried out at room temperature by using approximately 0.08 mmol of the Ir(OR)(cod)(PCy$_3$) complex and 0.08 mmol of phenol in 1 mL of CDCl$_3$. The ^{1}H NMR spectra showed a total conversion of the starting complex in all reactions. In a typical procedure, Ir(OEt)(cod)(PCy$_3$) (50 mg, 0.08 mmol) was dissolved in 1 mL of CDCl$_3$ and PhOH (8 mg, 0.08 mmol) was added. The solution was placed in a nitrogen-purged NMR tube; 15 min after mixing the compounds, the ^{1}H NMR spectrum showed only the resonances of Ir(OPh)(cod)(PCy$_3$) complex and EtOH.

Ir(C≡CPh)(cod)(PCy$_3$). A mixture of Ir(OEt)(cod)(PCy$_3$) (100 mg, 0.16 mmol) and HC≡CPh (37 μL, 0.33 mmol) in diethyl ether was left to react for 2 h. The resulting red solution was concentrated, and methanol was added to give a red precipitate that was filtered, washed with methanol, and dried under vacuum: yield 86 mg (78%). Anal. Calcd for $C_{34}H_{50}IrP$: C, 59.89; H, 7.39. Found: C, 59.61; H, 6.95. IR (Nujol): ν(C≡C) 2090 cm^{-1}. ^{1}H NMR (CDCl$_3$, ppm): 1.1–2.3 (m, 41 H, C_6H_{11}, >CH$_2$ (cod)), 3.65 (br, 2 H, =CH (cod)), 4.79 (br, 2 H, =CH (cod)), 7.06 (d, 1 H, J_{H-H} = 7 Hz, C_6H_5), 7.18 (t, 2 H, J_{H-H} = 7 Hz, C_6H_5), 7.28 (d, 2 H, J_{H-H} = 7 Hz, C_6H_5).

Determination and Refinement of the Structure. Crystals suitable for diffraction studies were obtained by cooling a solution of the complex in acetone to −20 °C. Crystal data are listed in Table I. The stability and orientation of the crystal were checked by measuring two standard reflections every 90 min. No significant variations were detected. An empirical absorption correction was applied.[26] In the final cycles of the refinement,

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weighting scheme was applied as to give no trends in $\langle w\Delta^2F\rangle$ vs $\langle F_o\rangle$ and $\langle(\sin\theta)/\lambda\rangle$, with $w = 1/\sigma_1{}^2\sigma_2{}^2$. ΔF were first least squares linearly adjusted to $|F_o|$, and the function taken as σ_1. Then $\Delta^2F/\sigma_1{}^2$ were fitted to $(\sin\theta)/\lambda$, and the function taken as $\sigma_2{}^2$. The final positional parameters of the non-hydrogen atoms are listed in Table III.

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Registry No. Ir(OMe)(cod)(PC_{y3}), 119694-74-5; Ir(OEt)(cod)(PC_{y3}), 119694-75-6; Ir(OPh)(cod)(PC_{y3}), 119694-76-7; Rh(OPh)(cod)(PC_{y3}), 119694-77-8; $IrH_5(PC_{y3})_2$, 65231-12-1; *mer*-$IrH_3(CO)(PC_{y3})$, 119694-78-9; $IrH_2(SiEt_3)(cod)(PC_{y3})$, 119720-77-3; $IrH_2(SiMe_2Ph)(cod)(PCy_3)$, 119694-79-0; Ir(C≡CPh)(cod)($PC_{]3}$), 119694-79-0; [Ir(μ-OMe)(Cod)]$_2$, 12148-71-9; [Ir(μ-OEt)(cod)]$_2$, 35429-65-3; [Ir(μ-OPh)(cod)]$_2$, 35429-67-5; [Rh(μ-OMe)(cod)]$_2$, 12148-72-0.

Supplementary Material Available: Tables of hydrogen parameters (Table IV), thermal factors (Table V), and bond lengths and angles (Table VII) (8 pages); a listing of structure factors (21 pages). Ordering information is given on any current masthead page.

X-ray Structure, Reactivity, and Catalytic Properties of a (Cyclopentadienone)ruthenium Dimer, $[(C_4Ph_4CO)(CO)_2Ru]_2$

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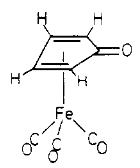
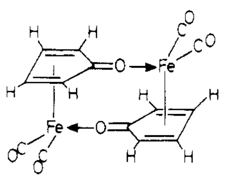
The title complex **4a** as well as several other isostructural complexes have been prepared. Single-crystal X-ray diffraction analysis of **4a** indicates a centrosymmetric dimeric structure (Figure 1); the complex crystallizes in space group $P\bar{1}$ (No. 2): a = 10.938 (1) Å, b = 11.990 (1) Å, c = 12.528 (1) Å, α = 68.62 (1)°, β = 77.99 (1)°, γ = 64.18 (1)°, V = 1374.8 (2) Å^3, Z = 2 (monomer units), 4835 unique reflections, R = 0.056, 4324 reflections, $F > 4\sigma(F)$. The cyclopentadienone carbonyl is bent back from the diene plane at an angle of 6.7°, with a >C=O bond length of 1.270 (7) Å. A crossover experiment with two structurally different dimer complexes indicates that the thermal dissociation of these dimers is a relatively low-energy process. Nucleophilic ligands, L (L = CO, phosphines, amines), react readily with **4a** to give mononuclear complexes of the type (η^4-C_4Ph_4CO)Ru(CO)$_2$L. Treatment of **4a** with either dihydrogen or ethanol leads to oxidative addition of dihydrogen to Ru with the formation of (η^5-C_4Ph_4COH)(CO)$_2$RuH. The catalytic activity of **4a** and other related complexes is discussed in the light of the above results.

Introduction

A complex with the empirical formula $C_7H_4O_3Fe$, first isolated by Reppe[1] from the reaction of acetylene with $Fe(CO)_5$, was formulated by Wilkinson et al.[2] and later also by others[3,4] as the centrosymmetric dimer **2**. Complex **2** is presumably formed under the reaction conditions by decarbonylation of (cyclopentadienone)tricarbonyliron (**1**). Although it was stated that an X-ray analysis of **2** had been undertaken,[3] to the best of our knowledge it has never been published. An extensive series of substituted (cyclopentadienone)tricarbonyliron complexes of type **1** was subsequently prepared by Weiss and Hübel,[5] but the transformation of these substituted complexes into dimers of type **2** was not reported.



1



2

A ruthenium complex, (tetraphenylcyclopentadienone)tricarbonylruthenium **3a**, analogous to the iron complex **1**, has been synthesized by two groups,[6,7] and its X-ray structure has been reported.[8] Bruce and Knight[7] have also prepared (tetrakis(trifluoromethyl)cyclopentadienone)tricarbonylruthenium. No attemps to convert these complexes to ruthenium dimers of type **4** were reported.

The chemical and in particular the catalytic properties of substituted cyclopentadienone (CPD) carbonyl ruthenium complexes have been reported by Shvo et al.[8-12] Complex **3a** (and later also **5**) was found to function as a catalyst precursor in several reactions, originally in the oxidative coupling of primary alcohols to esters and subsequently in the oxidation of secondary alcohols to ketones[9] and in various catalytic hydrogenations.[10] It was found that in these catalytic reactions, **3a** is transformed into a new isolable complex with ν(CO) at 2035, 2010, 1980, and 1970 (sh) cm^{-1} in KBr, which was initially assigned the molecular formula $[(C_4Ph_4CO)(CO)_2Ru]_2$ and the struc-

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