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program, Patterson and Fourier recycling, refined parameters 109, $R = 0.067$, $R_w = 0.063$ [$w = 1/\sigma^2(F) + 0.0007F^2$].

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Supplementary Material Available: A table of structure factors (Table S1) (10 pages). Ordering information is given on any current masthead page.

Formation of Iridalactones by CH_2–O Oxidative Addition of Propiolactone to Iridium(I)

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Propiolactone undergoes facile oxidative addition to low-valent electron-rich Ir(I) complexes. $(C_8H_{14})Ir(PMe_3)_3Cl$ (1) yields the structurally characterized iridalactone *mer*-$(CH_2CH_2CO_2)Ir(PMe_3)_3Cl$ (2) by cleavage of the CH_2–O bond. The reaction is first order in both the lactone and 1. A likely mechanism involves nucleophilic attack by a 16-electron iridium complex on the CH_2–O carbon atom. The structure of 2 has been determined crystallographically [space group $P2_1/c$; a = 13.184 (5) Å, b = 13.852 (2) Å, c = 12.761 (4) Å; β = 111.20 (5)°; Z = 4; R = 0.033 for 4882 reflections].

Introduction

As part of our interest in the reactivity of C–O bonds of small ring compounds with low-valent, electron-rich metal complexes[1] we have examined the possibility of C–O oxidative addition of lactones to Ir(I). Although metallalactones may be intermediates in various reactions catalyzed by transition-metal complexes involving generation or transformation of lactones, isolation of such complexes is not common and most examples involve group 10 metals.[2] Recently, a rhodalactone was isolated,[3] and its relevance to the transition-metal-catalyzed cyclization of alkynoic acids to alkylidene lactones probed.[4] Oxidative addition of allyl and phenyl esters was observed.[5]

To our knowledge, the only example of oxidative addition of a lactone to a transition metal [Pt(II)] resulting in an isolable metallalactone was reported recently[2a] while this work was in progress.

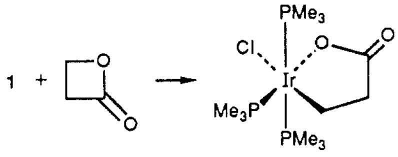
Since the complex $(C_8H_{14})Ir(PMe_3)_3Cl$ (1, C_8H_{14} = cyclooctene) is known to undergo facile C–O oxidative addition of epoxides,[1a] we have examined its reactivity, as well as the reactivity of other electron-rich Ir(I) complexes, with β-propiolactone. Indeed, five-membered iridalactones can be directly formed by oxidative addition of the CH–O bond of β-lactones to Ir(I).

Table I. Experimental Crystallographic Data for 2

mol wt	574.04
space group	$P2_1/c$ (monoclinic)
temp, °C	−183
cell constants	
a, Å	13.184 (5)
b, Å	13.852 (2)
c, Å	12.761 (4)
β, deg	111.20 (5)
cell vol, Å^3	2173 (1)
formula	$C_{12}H_{31}O_2P_3ClIr\cdot{}^1/_2(C_7H_8)$
formula units/unit cell	4
D(calcd), g cm^{-3}	1.7548
μ(calcd), cm^{-1}	64
diffractometer/scan	Rigaku AFC5/ω–2θ
source	rotating anode Rigaku RU300
speed of measmt, deg min^{-1}	10
radiation, graphite monochr	Mo K$\bar{\alpha}$ (I = 0.7114 Å)
max cryst dimens, mm	0.15 × 0.15 × 0.15
no. of reflections	
measured	4882
duplicates	402
with $F_o > 3\theta(F_c)$	3860
θ_{max}, deg	54
R_{sym}	0.02
final R,R_w	0.033, 0.043

Results and Discussion

Addition of β-propiolactone to a toluene solution of 1 at −30 °C, followed by warming to room temperature, results in complete conversion to the iridalactone complex 2 (eq 1). This reaction proceeds even at −30 °C (requiring



2

(1)

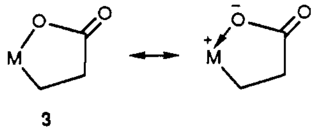


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Table II. Bond Distances (Å) and Angles (deg) for 2

	Bond Distances		
Ir(1)–Cl(2)	2.4863 (19)	P(4)–C(10)	1.8268 (73)
Ir(1)–P(3)	2.2432 (22)	P(4)–C(11)	1.8183 (84)
Ir(1)–P(4)	2.3364 (19)	P(5)–C(12)	1.8231 (76)
Ir(1)–P(5)	2.3438 (20)	P(5)–C(13)	1.8367 (62)
Ir(1)–O(15)	2.1242 (49)	P(5)–C(14)	1.8198 (90)
Ir(1)–C(19)	2.1194 (57)	O(15)–C(16)	1.3079 (71)
P(3)–C(16)	1.8317 (74)	C(16)–O(17)	1.2167 (90)
P(3)–C(7)	1.8252 (73)	C(16)–C(18)	1.5313 (97)
P(3)–C(8)	1.8169 (73)	C(18)–C(19)	1.5459 (115)
P(4)–C(9)	1.8315 (66)		
	Bond Angles		
O(15)–Ir(1)–C(19)	83.1 (2)	C(6)–P(3)–C(7)	102 (4)
P(5)–Ir(1)–C(19)	94.3 (2)	Ir(1)–P(4)–C(11)	109.7 (3)
P(5)–Ir(1)–O(15)	84.7 (1)	Ir(1)–P(4)–C(10)	121 (2)
P(4)–Ir(1)–C(19)	93.9 (2)	Ir(1)–P(4)–C(9)	116 (3)
P(4)–Ir(1)–O(15)	86.8 (1)	C(10)–P(4)–C(11)	103 (3)
P(4)–Ir(1)–P(5)	167.5 (1)	C(9)–P(4)–C(11)	101 (3)
P(3)–Ir(1)–C(19)	89.9 (2)	C(9)–P(4)–C(10)	103.1 (3)
P(3)–Ir(1)–O(15)	172.8 (1)	Ir(1)–P(5)–C(14)	117 (3)
P(3)–Ir(1)–P(5)	94.5 (1)	Ir(1)–P(5)–C(13)	120 (3)
P(3)–Ir(1)–P(4)	95 (1)	Ir(1)–P(5)–C(12)	107.6 (2)
Cl(2)–Ir(1)–C(19)	172 (2)	C(13)–P(5)–C(14)	104.8 (4)
Cl(2)–Ir(1)–O(15)	88.4 (1)	C(12)–P(5)–C(14)	102 (3)
Cl(2)–Ir(1)–P(5)	84.7 (1)	C(12)–P(5)–C(13)	104 (3)
Cl(2)–Ir(1)–P(4)	85.8 (1)	Ir(1)–O(15)–C(16)	115 (4)
Cl(2)–Ir(1)–P(3)	98 (1)	O(15)–C(16)–C(18)	115 (6)
Ir(1)–P(3)–C(8)	115 (2)	O(15)–C(16)–O(17)	123 (6)
Ir(1)–P(3)–C(7)	117 (2)	O(17)–C(16)–C(18)	121 (7)
Ir(1)–P(3)–C(6)	117 (3)	C(16)–C(18)–C(19)	115 (6)
C(7)–P(3)–C(8)	104 (4)	Ir(1)–C(19)–C(18)	106.3 (4)
C(6)–P(3)–C(8)	99 (3)		

several hours for completion) and is much faster than the corresponding reaction of the platinum complex $PtMe_2$(NN) (NN = 1,10-phenanthroline).

In accordance with this, **1** also undergoes facile oxidative addition of β-butyrolactone, yielding a mixture of products, whereas the above-mentioned platinum complex does not react with this substrate.[2a]

The structure of **2** was determined by ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR and IR spectroscopies and is confirmed by a single-crystal X-ray diffraction study on crystals grown by slow evaporation of the solvent from a toluene solution.

As expected (Figure 1 and Tables I and II), a distorted octahedral structure is obtained with the two trans phosphines tilted toward the less hindered Ir–O–C plane. The Ir–P bond trans to PMe_3 is significantly longer (by 0.1 Å) than that trans to O, thus reflecting the much larger trans effect of the phosphine ligand. Interestingly, **2** exhibits a considerably shorter C=O and longer C–O bond than in the analogous complex $PtMe_2[CH_2CH_2C(O)O]$(NN) (NN = 1,10-phenanthroline) where the two bonds are equal in length. This probably reflects a larger contribution of the resonance form **3** in the case of **2**, perhaps because of the possibility of back donation to the phosphine ligands.

It is noteworthy that exclusive cleavage of the CH_2–O rather than the OC–O bond occurred. Both modes of nucleophilic cleavage of β-propiolactone are known,[6] with attack at the alkyl carbon resulting in more strain relief in the transition state. Reactions of propiolactone with Pt(II)[2a] and Ni(0)[2g] also result in alkyl–oxygen bond cleavage, although a metallalactone was not isolated in the latter case.

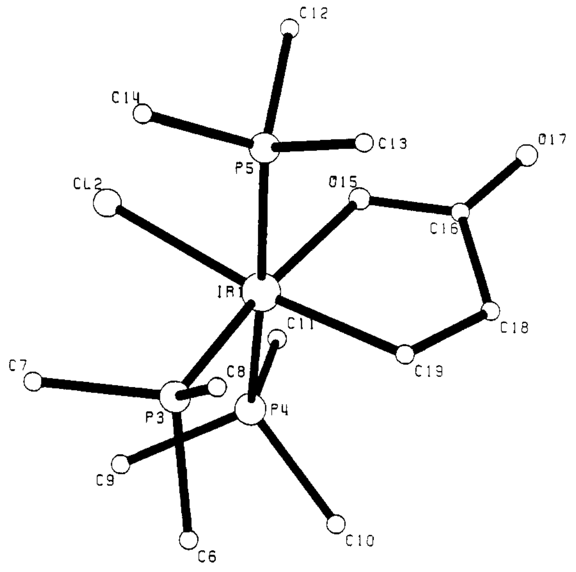
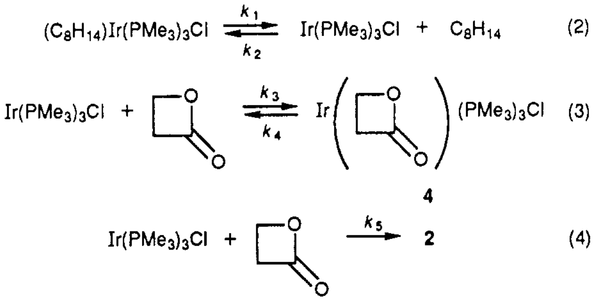


Figure 1. Pluto drawing of a molecule of **2**.

Reaction of **1** with β-propiolactone can be conveniently followed by ^{1}H NMR (observing lactone disappearance) and by $^{31}P\{^1H\}$ NMR (observing disappearance of **1** and formation of **2**).

Compound **1** undergoes facile dissociation of the cyclooctene ligand in solution[7] (eq 2). Upon addition of the



lactone at −30 °C, immediate disappearance of $Ir(PMe_3)_3Cl$ and the lactone takes place to form a new complex (exhibiting $^{31}P\{^1H\}$ NMR δ −35 (t, J = 16 Hz, 1 P), −52 (d, J = 16 Hz, 2 P). This complex is likely to be a pentacoordinate lactone complex **4** (eq 3). The position of equilibrium 3 is shifted to the left at higher temperatures [K(21 °C) = 2].

Reaction 1 exhibits first-order kinetics in both **1** and the lactone with k_{obsd}(21 °C) = 2.3×10^{-3} L mol^{-1} s^{-1} (in toluene-d_8). Apparently, the facile equilibria involving cyclooctene dissociation from **1** and lactone coordination do not have a significant effect on the overall reaction rate. A typical conversion plot is illustrated in Figure 2.

The theoretical lines are derived by using the simple model described by eqs 2–4 in an iterative kinetic modeling program, GIT, which combines statistical comparison of experimental data with a GEAR-generated theoretical model.[8] A model in which complex **4** lies in the reaction pathway to **2** leads to an unacceptable fit.

Other Ir complexes also react with β-propiolactone, leading to the following order of reactivity: **1** > $Ir(PEt_3)_3Cl$ > $Ir(PMe_3)_4{}^+PF_6{}^-$ ≫ $Ir(PEt_3)_2(C_2H_4)_2Cl$ > $Ir(PMe_3)_2(CO)Cl$.

This indicates (a) higher reactivity for higher electron density on the metal, as expected for reactions involving

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[7] Milstein, D. To be published.

[8] Weigert, F. *J. Comput. Chem.* **1987**, *11*, 273.

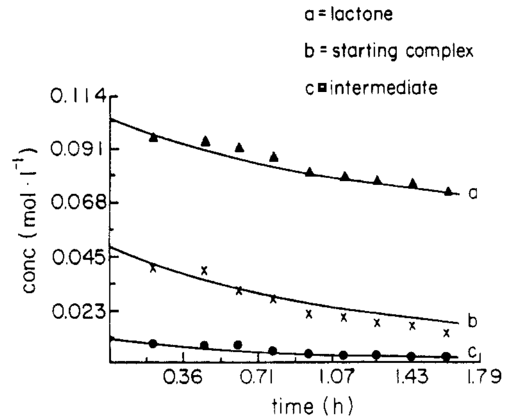
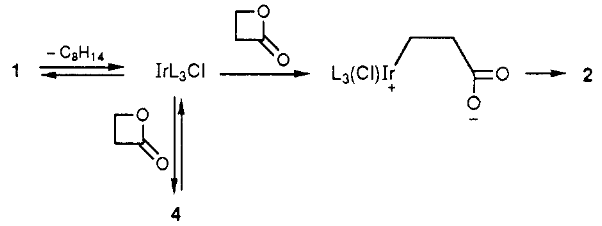


Figure 2. Conversion plot for reaction 1. Solid lines represent a theoretical fit of the experimental data based on eqs 2–4.

Scheme I



a rate-determining oxidative-addition step; (b) importance of steric factors; (c) plausible involvement of a 16-electron complex in the oxidative addition step, rather than the 14-electron intermediate frequently invoked in various oxidative-addition reactions of Ir(I) and Rh(I) phosphine complexes.[9] If such an intermediate was important here, $Ir(PEt_3)_3Cl$ and $Ir(C_2H_4)_2(PEt_3)_2Cl$ would be expected to react at similar rates since both would involve $Ir(PEt_3)_2Cl$ as the active species.[10] Similar reaction rates of $Ir(PEt_3)_3Cl$ and $Ir(PEt_3)_2(C_2H_4)_2Cl$ are indeed observed in N–H oxidative addition which is thought to involve a 14-electron complex.[11]

A plausible mechanistic outline for reaction 1 involving nucleophilic cleavage of the lactone is shown in Scheme I.

Experimental Section

General Procedures. All the reactions were carried out under nitrogen in a Vacuum Atmospheres glovebox equipped with a recirculation "Dri-Train". Solvents were dried, distilled, and degassed before introduction into the glovebox, where they were stored over activated 4-Å molecular sieves. Reaction flasks were washed with water and acetone and then oven-dried before introducing them into the glovebox.

β-Butyrolactone was vacuum distilled before use, and β-propiolactone was used as supplied from Aldrich.

Spectroscopic Analysis. NMR spectra were recorded on Bruker WH-270 or AM-500 instruments. ^{1}H nuclei were observed at 270 or 500 MHz; ^{31}P nuclei were observed at 109.294 MHz (with ^{1}H decoupling). IR spectra were recorded in Nujol mulls on KBr plates on a Matteson Cygnus-25 or on a Nicolet MX-1 spectrometer. ^{1}H NMR chemical shifts are relative to tetramethylsilane; the residual solvent peak was used as an internal reference. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at δ 0.0 (external reference), with shifts downfield of the reference considered positive. $(C_8H_{14})Ir(PMe_3)_3Cl$[13] and $Ir(PMe_3)_4{}^+PF_6{}^-$[12] were prepared according to a modification of the published procedure. $Ir(PMe_3)_2(CO)Cl$[14] and $Ir(PEt_3)_2(C_2H_4)_2Cl$[11] were prepared as reported.

***mer*-$[CH_2CH_2COO]Ir(PMe_3)_3Cl$ (2).** To a solution of $(C_8H_{14})Ir(PMe_3)_3Cl$ (290 mg, 0.512 mmol) in 5 mL of toluene was added dropwise, with stirring, a solution of β-propiolactone (37 mg, 0.513 mmol) in 2 mL of toluene, both solutions at −30 °C. The deep red solution of the complex turned first yellow and became colorless after 30 min of warming to room temperature. The precipitate formed was separated from the mother liquor by decantation, washed with cold toluene, and dried under high vacuum, yielding pale yellow microcrystalline *mer*-$[CH_2CH_2COO]Ir(PMe_3)_3Cl$ (192 mg, 59%): IR (Nujol) 1621 (s, C=O), 950 (s, PMe_3) cm^{-1}; ^{1}H NMR (pyridine-d_5) δ 1.41 (d, J_{P-H} = 10 Hz, 9 H, PMe_3), 1.49 (t, J_{P-H} = 6.3 Hz, 18 H, 2 PMe_3), 2.60 (t, J = 7.8 Hz, 4 H, $[(CH_2)_2]$); $^{31}P\{^1H\}$ NMR (pyridine-d_5) δ −34 (d, $J_{P-P'}$ = 21.6 Hz, 2 P), −49.39 (t, $J_{P-P'}$ = 21.6 Hz, 1 P); $^{13}C\{^1H\}$ NMR (pyridine-d_5) δ −15 (d, J = 3.4 Hz, Ir–C), 9 (t, J_{P-C} = 16 Hz, 2 PMe_3), 15 (d, J_{P-C} = 35 Hz, 1 PMe_3), 36.5 (s, CH_2CO), 186 (s, CO).

Reactions of Other Iridium Complexes with β-Propiolactones. The procedure was the same as for 1 except that in the case of $Ir(PEt_3)_2(C_2H_4)_2Cl$ and $Ir(PMe_3)_2(CO)Cl$, no reaction occurred after 1 day at room temperature (according to IR and $^{31}P\{^1H\}$ NMR).

In the case of $Ir(PEt_3)_3Cl$, after 18 h of reaction 16% of the starting material is converted into a new complex, exhibiting the following: $^{31}P\{^1H\}$ NMR δ −9.5 (d, $J_{P-P'}$ = 19 Hz, 2 P), −21 (t, $J_{P-P'}$ = 19 Hz, 1 P). With $Ir(PMe_3)_4{}^+PF_6{}^-$ 14% of the starting material is converted into a mixture of products after 18 h of reaction (according to $^{31}P\{^1H\}$ NMR).

Kinetic Measurements. The procedure was the same except that a larger excess of lactone was used in this case (33 mg (0.458 mmol) of lactone for 114 mg (0.201 mmol) of 1) and the solvent used was toluene-d_8. Immediately after the solutions were mixed, the NMR tube was taken in a Dewar container at −70 °C to the NMR spectrometer.

Crystal Structure Determination of 2.[15] A single crystal (dimensions 0.15 × 0.15 × 0.15 mm) grown by slow evaporation of a toluene solution was mounted on the diffractometer equipped with a low-temperature device.

Absorption correction was performed according to Walker and Stuart.[16]

A summary of data collection parameters is given in Table I. The hydrogen atoms were found from the difference Fourier map and refined with an overall temperature factor (U_{iso} = 0.032 Å^2). Refinement of the non-hydrogen atoms was done with an overall temperature factor (U_{iso} = 0.032 Å^2). Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of R = 0.033 and R_w = 0.043.

Acknowledgment. This research was supported by the Fund for Basic Research administered by the Israel Academy of Sciences and Humanitites. We thank the Du Pont Co., USA, for generous gifts of chemicals and supplies.

Supplementary Material Available: Tables of the final fractional coordinates, thermal parameters, and torsional angles (6 pages); a listing of observed and calculated structure factors for 2 (11 pages). Ordering information is given on any current masthead page.

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(9) See, for example: (a) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 129. (b) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436.

(10) We have observed that $Ir(C_2H_4)_2(PEt_3)_2Cl$ readily dissociates one ethylene ligand in solution and assume that dissociation of the second ethylene ligand is fast compared to C–O oxidative addition.

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(13) Herskovitz, T. *Inorg. Synth.* **1982**, 21, 99.

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