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Acetylacetonato(phosphane)iridium Complexes: Synthesis and Catalytic Activity in the Cyclization of Alkynoic Acids

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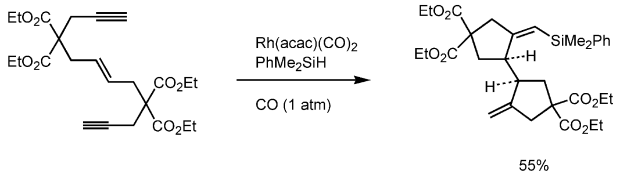
Dedicated to the memory of Keith Fagnou

Keywords: Iridium / Phosphane ligands / Cyclization / Lactones

The iridium complex [Ir(acac)(η^2-coe)$_2$] (**1**) has been easily prepared by the addition of Tl(acac) to a suspension of [Ir(μ-Cl)(η^2-coe)$_2$]$_2$ in hexane. Complex **1** has been characterized fully including an X-ray diffraction study. It is moderately stable and is a useful precursor to a number of different acetylacetonato(phosphane)iridium complexes via addition of monodentate and bidentate phosphanes. Reactions proceeded at room temperature to give high yields of the desired square planar phosphane complexes [Ir(acac)(P)] (**2**: P = 2 PPh_3, **3**: P = 2 $PMePh_2$, **4**: P = dppm, **5**: P = dppe, **6**: P = dppp, **7**: P = dppb, **8**: P = dppf, **9**: P = dcpe) except for those involving dppe, which gave a complicated mixture of products. Complex [Ir(acac)(dppe)] (**5**) was prepared in a microwave reactor at 125 °C. All complexes prepared in this study were efficient in the intramolecular catalyzed cyclization of 4-pentynoic acid to give exclusive formation of the exocyclic γ-methylene-γ-butyrolactone. Complex **1** was found to be the most active and selective catalyst precursor for the intramolecular cyclization of both 4-pentynoic acid and 5-hexynoic acid.

Introduction

Transition metals have been employed as catalysts for industrial processes as early as the 19th century[1] and are currently used in the manufacture of bulk chemicals such as *n*-butanal (hydroformylation) and acetic acid (carbonylation), as well as in the generation of fine or specialty chemicals. While the development of novel catalysts is the subject of intense research, acetylacetonato(acac)-metal complexes have always played a predominant role in this economically and environmentally important area of chemistry. For instance, one of the areas where β-diketonato-metal complexes have made significant contributions in the last few years has been in the catalyzed hydroformylation reaction.[2] Although $RhH(CO)(PPh_3)_3$ is widely recognized as one of the most versatile catalysts for the hydroformylation reaction, the ease of synthesis, stability and ability to fine tune the electronic and steric environments around the metal center by the addition of ligands makes complexes of the type Rh(acac)$(CO)_2$ and Rh(acac)$(H_2C{=}CH_2)_2$ valuable precatalysts for this reaction.[3] Most of the work in this area has involved reactions using modified phosphane and phosphite derivatives. Indeed, van Leeuwen and co-workers found that bulky monodentate phosphite/rhodium systems are highly active and selective hydroformylation catalysts for a wide range of substrates, including di- and trisubstituted alkenes.[3l] Acetylacetonatorhodium complexes also play an important role in the field of metal-catalyzed cyclization or cycloaddition reactions. For example, Ojima and co-workers have reported that derivatives of Rh(acac)-$(CO)_2$ catalyze the silane-initiated cyclization of enediynes to give the corresponding biscyclopentyl products in excellent yields (Scheme 1).[4]



Scheme 1. The acetylacetonatorhodium cyclization of enediynes.

While acetylacetonato(phosphane)rhodium complexes have been well studied in terms of synthesis, structure and activities, it is somewhat surprising that the analogous chemistry and potential catalytic properties of the iridium complexes have not yet been fully explored. The iridium complex [Ir(acac)$(CO)_2$] has been used to generate other organometallic complexes or clusters[5] and its oxidative addition chemistry with perfluoroalkyl iodides has been recently investigated in an elegant study by Hughes and co-workers.[6] However, very little is known about acetylace-

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tonatoiridium complexes containing phosphane ligands.[7] Therefore we have decided to investigate the synthesis and characterization of these species and examine their potential to act as precatalysts in the cyclization of alkynoic acids, the results of which are reported within.

Results and Discussion

Synthesis and Characterization of Iridium Complexes

Although a new synthetic route to the ethylene compound [Ir(acac)(η^2-H_2C=CH_2)$_2$] has recently been prepared,[8] relatively low yields (45%) and thermal instability at room temperature does not make this compound an ideal starting material for substitution reactions. We therefore decided to prepare the iridium complex [Ir(acac)(η^2-coe)$_2$] (**1**) (coe = *cis*-cyclooctene = C_8H_{14}) by the addition of Tl(acac) to a hexane suspension of [Ir(μ-Cl)(η^2-coe)$_2$]$_2$.[9] Complex **1** was prepared in good yields at room temperature (18 h) and crystals of **1** suitable for a single-crystal X-ray diffraction study were grown from hexane at room temperature, the structure of which is shown in Figure 1. The iridium oxygen bond lengths of Ir(1)–O(1) 2.0598(19) and Ir(1)–O(2) 2.0521(19) Å are similar to those observed in the ethylene complex [Ir(acac)(η^2-H_2C=CH_2)$_2$] and other acetylacetonatoiridium complexes.[10] Likewise, the C=C double bonds of the cyclooctene group are slightly elongated at C(6)–C(7) 1.414(4) and C(14)–C(15) 1.422(4) Å compared to 1.404(4) Å seen in [Ir(acac)(η^2-H_2C=CH_2)$_2$].[8] The isostructural rhodium analog Rh(acac)(η^2-coe)$_2$ also displayed somewhat shorter alkene bonds at 1.402(3) and 1.405(3) Å,[11] which may signify a slight increase in backbonding into the alkene π* ligands on replacing rhodium with iridium.

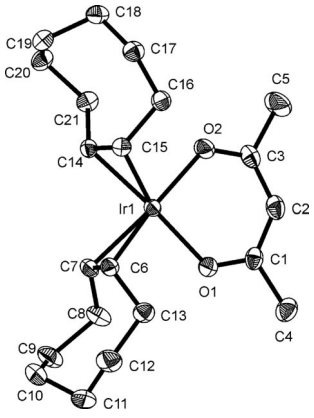


Figure 1. Molecular structure of **1** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(1) 2.0598(19), Ir(1)–O(2) 2.0521(19), Ir(1)–C(14) 2.117(3), Ir(1)–C(7) 2.120(2), Ir(1)–C(6) 2.125(3), Ir(1)–C(15) 2.129(3), C(6)–C(7) 1.414(4), C(14)–C(15) 1.422(4); O(2)–Ir(1)–O(1) 88.31(8), O(2)–Ir(1)–C(14) 90.28(9), O(1)–Ir(1)–C(14) 166.47(9), O(2)–Ir(1)–C(7) 153.82(10), O(1)–Ir(1)–C(7) 88.42(9), C(14)–Ir(1)–C(7) 86.92(10), O(2)–Ir(1)–C(6) 167.14(10), O(1)–Ir(1)–C(6) 91.04(9), C(14)–Ir(1)–C(6) 93.29(10), C(7)–Ir(1)–C(6) 38.91(10), O(2)–Ir(1)–C(15) 88.21(9), O(1)–Ir(1)–C(15) 154.15(10), C(14)–Ir(1)–C(15) 39.13(10).

While Esteruelas[7b–7d] and Werner[7e,7f] have carried out elaborate studies on [Ir(acac)(η^2-H_2C=CH_2)(PCy_3)] (Cy = cyclohexyl) and [Ir(acac)(η^2-H_2C=CH_2)(P*i*Pr_3)], respectively, much less is known about complexes containing two monodentate phosphane ligands or bidentate phosphanes. For instance, Eisenberg reported the synthesis of [Ir(acac)-(PPh_3)$_2$] (**2**) in 1984 but little is known about its chemistry and catalytic abilities.[7a] In a more recent study, Hughes and co-workers have found that [Ir(acac)(PMe_3)$_2$] reacts at room temperature with 1,2,3-triphenyl-3-vinylcyclopropene to give an unusual 1,2,4-triphenyliridacyclohexadiene complex containing *cis*-phosphane ligands.[7g] In this study we have made **2** via the addition of two equivalents of PPh_3 to **1** in high yield (94%). Analogous reactions with methyldiphenylphosphane gave the corresponding complex [Ir-(acac)($PMePh_2$)$_2$] (**3**) in yields of 83%. Complex **3** has been characterized by a number of physical methods including multinuclear NMR spectroscopy. As expected, a doublet is observed in the ^{1}H NMR spectra at δ = 1.71 ppm (J_{HP} = 8.4 Hz) for the phosphane methyl group and the ^{31}P{^{1}H} NMR spectra shows a singlet at δ = –1.6 ppm. The formation of **3** has also been confirmed by a single-crystal X-ray diffraction study (Figure 2). The molecular structure of **3** has a center of symmetry where the Ir(1)–P(1) distance of 2.2061(5) Å is typical of those observed in other iridium-$PMePh_2$ structures.[12] Likewise, the bond lengths within the acac ring are similar to those reported previously[10] (Table 1).

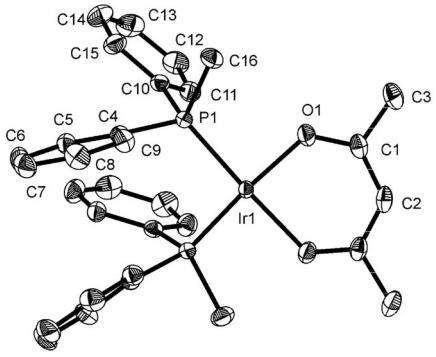


Figure 2. Molecular structure of **3** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(1) 2.0678(14), Ir(1)–P(1) 2.2061(5), P(1)–C(10) 1.831(2), P(1)–C(16) 1.832(2), P(1)–C(4) 1.8334(19), O(1)–C(1) 1.277(2); O(1)#1–Ir(1)–O(1) 88.08(8), O(1)#1–Ir(1)–P(1) 175.04(4), O(1)–Ir(1)–P(1) 87.92(4), O(1)#1–Ir(1)–P(1)#1 87.92(4), O(1)–Ir(1)–P(1)#1175.04(4), P(1)–Ir(1)–P(1)#196.22(3).

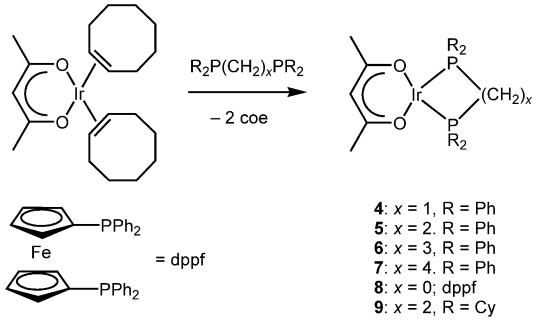
The iridium complexes **4**–**9** were prepared readily by the addition of the diphosphane to solutions of **1** in toluene or THF (Scheme 2). Once again all new compounds have been characterized fully, and spectroscopic data is consistent with analogous acetylacetonatoiridium derivatives[10] and the corresponding acetylacetonato(phosphane)rhodium compounds.[13] X-ray diffraction studies were also carried out for complexes **4** (Figure 3, a), **6** (Figure 3, b), and **9** (Figure 4). The iridium atoms assume a slightly distorted square planar configuration with Ir–P distances of

Table 1. Crystallographic data collection parameters for **1**, **3**, **4**, **6**, **9**, and **10**.

Complex	**1**	**3**	**4**	**6**	**9**	**10**
Formula	$C_{21}H_{35}IrO_2$	$C_{31}H_{33}IrO_2P_2$	$C_{30}H_{29}IrO_2P_2 \cdot 0.5\ C_6H_{14}$	$C_{38}H_{39}IrO_2P_2$	$C_{31}H_{55}IrO_2P_2$	$[C_{52}H_{48}IrP_4]\ Cl \cdot 2CHCl_3$
Formula mass	511.69	691.71	718.76	781.83	713.89	1263.17
Crystal dimensions /mm^3	$0.425 \times 0.35 \times 0.275$	$0.50 \times 0.35 \times 0.28$	$0.40 \times 0.40 \times 0.15$	$0.30 \times 0.20 \times 0.17$	$0.45 \times 0.25 \times 0.25$	$0.50 \times 0.40 \times 0.20$
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/c$	$C2/c$	$P\bar{1}$
Z	2	4	4	4	8	1
a /Å	10.2741(13)	19.575(2)	17.373(2)	19.7378(16)	32.632(5)	10.6165(8)
b /Å	11.1866(15)	10.9709(10)	11.2795(12)	12.0941(10)	11.4377(16)	12.0141(9)
c /Å	11.3708(15)	14.9089(16)	17.460(3)	13.9907(12)	17.174(3)	12.2891(9)
α /°	103.956(1)	90	90	90	90	117.314(1)
β /°	113.087(1)	121.361(2)	119.630(2)	97.4220(10)	92.075(3)	102.331(1)
γ /°	108.973(1)	90	90	90	90	95.470(1)
Volume /Å^3	1029.8(2)	2734.1(5)	2974.0(7)	3311.8(5)	6405.9(16)	1326.38(17)
$D_{calcd.}$ /mg m^{-3}	1.650	1.680	1.605	1.568	1.480	1.581
T /K	173(1)	173(1)	173(1)	173(1)	223(1)	173(1)
Radiation	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)	Mo-K_α (λ = 0.71073 Å)
μ /mm^{-1}	6.493	5.027	4.625	4.160	4.293	3.026
Total reflections	7128	9275	20286	22829	21990	9079
No. of variables	219	166	318	390	327	331
θ (°)	2.13 to 27.49	2.22 to 27.49	1.35 to 27.50	1.04 to 27.49	1.89 to 27.50	1.95 to 27.50
GoF on F^2	1.085	1.121	0.996	1.112	1.056	1.057
R_1[a] [$I > 2\sigma(I)$]	0.0178	0.0149	0.0249	0.0196	0.0189	0.0247
wR_2[b] (all data)	0.0469	0.0377	0.0542	0.0495	0.0487	0.0636
Largest diff peak & hole /Å	1.083 and –1.320	0.698 and –0.717	1.339 and –0.620	0.755 and –0.391	0.935 and –0.279	2.331 and –0.869

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[F_o^4]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0274 * P)^2 + (0.6485 * P)]$ (**1**), $1/[\sigma^2(F_o^2) + (0.0186 * P)^2 + (1.9667 * P)]$ (**3**), $1/[\sigma^2(F_o^2) + (0.0281 * P)^2]$ (**4**), $1/[\sigma^2(F_o^2) + (0.0713 * P)^2 + (2.0278 * P)]$ (**6**), $1/[\sigma^2(F_o^2) + (0.0239 * P)^2 + (3.7666 * P)]$ (**9**) and $1/[\sigma^2(F_o^2) + (0.0440 * P)^2 + (0.5245 * P)]$ (**10**); where $P = [\max(F_o^2, 0) + 2*F_c^2]/3$.

2.1890(9), 2.1764(7) Å (**4**), 2.1823(6), 2.1831(7) Å (**6**), and 2.1763(6), 2.1799(7) Å for the cyclohexyl derivative **9**. As with the analogous rhodium complexes,[14] iridium compounds **4**–**9** appear to be unstable in chlorinated solvents as C–Cl bond activation to give a mixture of products was observed after 24 h at room temperature.



Scheme 2. Synthesis of acetylacetonatoiridium complexes containing bidentate phosphanes.

Of singular interest in this study were attempts to generate the diphos derivative [Ir(acac)(dppe)] {**5**, dppe = 1,2-bis(diphenylphosphanyl)ethane}, which gave a mixture of products when reactions were carried out at room temperature. One of the products identified from this mixture appears to be the cationic species $[Ir(dppe)_2]^+$, where the counterion is presumably acac$^-$. Similar reactivity has been reported during attempts to make $[(\eta^5\text{-}C_9H_7)Ir(diphosphane)]$ via the displacement of the diolefin from $[(\eta^5\text{-}C_9H_7)Ir(\eta^4\text{-cod})]$ (where cod = 1,5-cyclooctadiene) or $[(\eta^5\text{-}C_9H_7)Ir(\eta^2\text{-coe})_2]$ with chiral diphosphanes.[15] Complexes of the type $[Ir(diphosphane)_2]^+$ were said to be the major species formed in these reactions, although the nature of the anion was not discussed in any significant detail. Also relevant is the study by Leitner and co-workers who found that addition of diphosphanes to Rh(hfacac)(η^4-cod) (hfacac = hexafluoroacetylacetonato anion) or Rh(hfacac)-(diphosphane) afforded complexes of the type [Rh(diphosphane)$_2$][hfacac].[16] To confirm that we were generating $[Ir(dppe)_2]^+$ in this work, we independently prepared the chloride derivative [[Ir(dppe)$_2$]Cl] (**10**). Spectroscopic data are consistent with known analogs and confirms the formation of these cations in solution.[17] A single-crystal X-ray diffraction study on **10** (Figure 5) was carried out and shows the iridium atom in a slightly distorted square planar configuration with Ir–P distances of 2.2988(6) and 2.3003(7) Å. Although typical for other $[Ir(diphosphane)_2]^+$ cations,[18] these bonds are slightly elongated with respect to the acac complexes in accord with the *trans* directing series. The coordinated acac species **5** could be prepared in high yields, however, but only at higher temperatures or using a microwave reactor.[19] Interestingly, this type of reactivity was specific only for the dppe case as all other diphosphanes proceeded smoothly over 18 h to give the corresponding neutral products in high yields, without the observance of any of the cationic species.

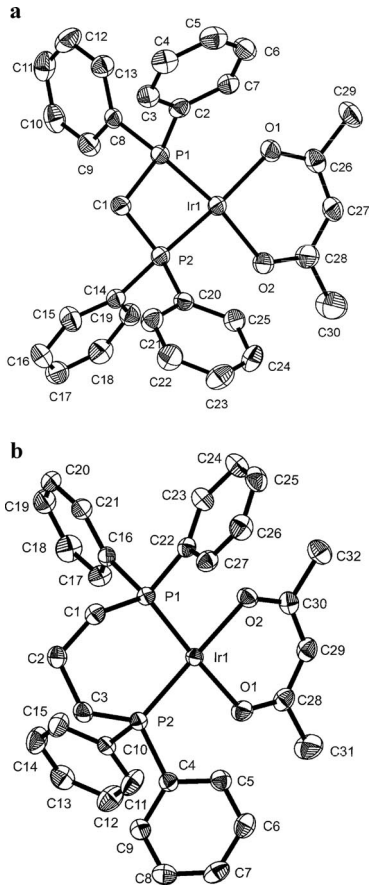


Figure 3. (a) Molecular structure of **4** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(2) 2.070(2), Ir(1)–O(1) 2.075(2), Ir(1)–P(2) 2.1764(7), Ir(1)–P(1) 2.1890(9); O(2)–Ir(1)–O(1) 88.68(8), O(2)–Ir(1)–P(2) 98.13(6), O(1)–Ir(1)–P(2) 170.93(7), O(2)–Ir(1)–P(1) 171.35(6), O(1)–Ir(1)–P(1) 99.96(7), P(2)–Ir(1)–P(1) 73.31(3). (b) Molecular structure of **6** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(2) 2.0682(18), Ir(1)–O(1) 2.0759(17), Ir(1)–P(1) 2.1823(6), Ir(1)–P(2) 2.1831(7); O(2)–Ir(1)–O(1) 88.56(7), O(2)–Ir(1)–P(1) 87.91(5), O(1)–Ir(1)–P(1) 175.88(5), O(2)–Ir(1)–P(2) 176.79(5), O(1)–Ir(1)–P(2) 89.33(5), P(1)–Ir(1)–P(2) 94.10(3).

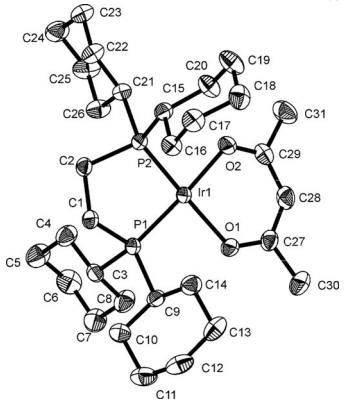


Figure 4. Molecular structure of **9** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–O(2) 2.0761(16), Ir(1)–O(1) 2.0856(17), Ir(1)–P(1) 2.1763(6), Ir(1)–P(2) 2.1799(7); O(2)–Ir(1)–O(1) 89.01(7), O(2)–Ir(1)–P(1) 172.97(5), O(1)–Ir(1)–P(1) 92.45(5), O(2)–Ir(1)–P(2) 92.70(5), O(1)–Ir(1)–P(2) 172.51(5), P(1)–Ir(1)–P(2) 86.74(2).

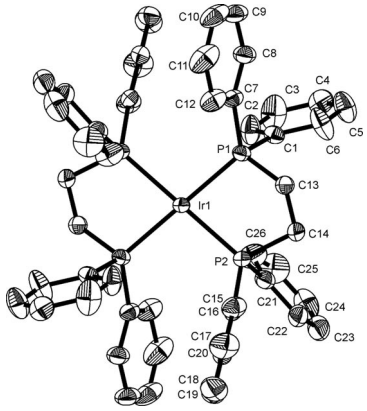
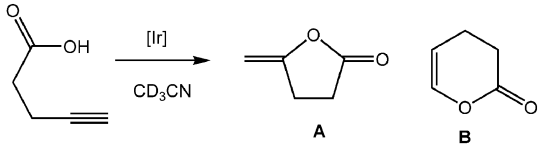


Figure 5. Molecular structure of the cation in **10** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir(1)–P(1) 2.2988(6), Ir(1)–P(2) 2.3003(7); P(1)–Ir(1)–P(1)#1 180.0, P(1)–Ir(1)–P(2) 82.38(2), P(1)#1-Ir(1)–P(2) 97.62(2).

Catalyzed Intramolecular Hydroalkoxylation

Catalysis with acetylacetonatoiridium compounds remains a largely unexplored area,[20] but recent studies have found that these complexes show promise in a number of organic transformations including the [2+2] cycloaddition of oxabicyclic alkenes with terminal alkynes.[20a] Related studies have also shown that iridium complexes can be used to effectively catalyze the synthesis of five- and six-membered oxygen-containing heterocycles from a number of unsaturated organic substrates.[21] The resulting heterocycles are prevalent in natural products and have numerous applications in pharmaceuticals, agricultural, fragrance and flavour chemicals. Elegant studies by Messerle and co-workers have found that cationic[22a] and neutral[22b] rhodium and iridium compounds can be used for the intramolecular cyclization of 4-pentynoic acid to give γ-methylene-γ-butyrolactone. With this in mind, we have investigated compounds **1**–**9** for their ability to catalyze this potentially useful transformation (Scheme 3).



Scheme 3. The iridium catalyzed intramolecular cyclization of 4-pentynoic acid.

Preliminary studies of 4-pentynoic acid were performed on an NMR scale using CD_3CN as a solvent and 5 mol-% catalyst at room temperature. The reaction progress was monitored by ^1H NMR spectroscopy and conversion of 4-pentynoic acid was determined by integration of product resonances relative to substrate resonances and 1,2-dimethoxybenzene as an internal standard. In all cases

complete conversion of the unsaturated substrate to give the desired γ-methylene-γ-butyrolactone **A** was observed. A more in depth study with representative iridium complexes **1**, **3** and **7** showed that reactions employing the cyclooctene precursor **1** were complete within 12 hours (Figure 6). Slightly shorter reaction times occurred with the monodentate phosphane complex **3** compared to the bidentate system **7**, where addition of phosphane appears to retard reaction rates. Indeed, reactions using **7** and an additional equivalent of dppb ligand proceeded with only 25% conversion at room temperature after 24 hours. Upon completion of catalysis, no free phosphane was observed in solution by ^{31}P NMR spectroscopy. Although these rates are somewhat slower than those observed by Messerle and co-workers using Rh^{I}/Ir^{I} indolyl complexes, these results show promise as the formation of the six-membered lactone ring **B**, as an unwanted side product, was not observed to any extent in reactions carried out at room temperature. A remarkable study by Valerga and co-workers has shown that complete reversal of regioselectivity in favour of the endocyclic lactone **B** can be achieved in reactions using σ-enynyl complex [TpRu{C(Ph)=C(Ph)C≡CPh}(PMe*i*Pr$_2$)] {Tp = hydrotris(pyrazolyl)borate(1–)} as the catalyst precursor.[21g]

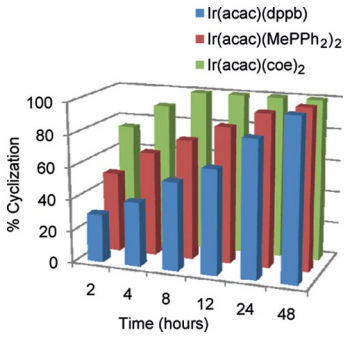
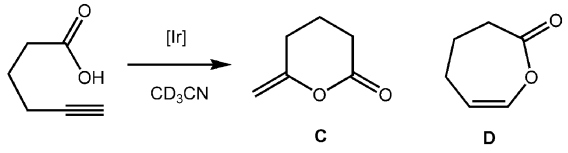


Figure 6. Cyclization of 4-pentynoic acid using iridium complexes **1**, **3**, and **7** at room temperature. Reactions monitored by ^1H NMR spectroscopy and product conversion confirmed by GC/MS.

Selectivity in favour of the five-membered ring (>99%) was also observed in reactions conducted at elevated temperatures (T = 100 °C, t = 20 min) using a catalytic amount of **1**. Reactions with catalyst precursors **3** and **7** proceeded at 100 °C (t = 1 h) and gave only minor amounts of the six-membered product **B** (<2%).

To expand the scope of these reactions, we then decided to investigate analogous cyclizations of 5-hexynoic acid (see Scheme 4). Reactions with this substrate are notoriously difficult and long reaction times are usually required. For example, reactions using a cationic rhodium dicarbonyl complex containing *N*-heterocyclic carbenes as a catalyst precursor does not exceed conversions of 80% after 8 days at 50 °C.[22a] Slightly better results have been achieved using rhodium trinuclear complexes with tris-carbene ligands, which gave 90% of the desired 6-methylidenetetrahydro-2-pyrone **C** after 5 days at 50 °C.[21c] A more recent study using catalytic amounts of $AuCl/K_2CO_3$ reported that the desired lactone could be generated selectively at room temperature after only two hours.[21a] In this study, we have re-examined the three representative iridium compounds and found that only the bis cyclooctene complex **1** was efficient in this transformation at room temperature (Figure 7). Although taking 72 h for complete conversion to take place, this reaction was remarkably selective in the formation of the desired six-membered ring lactone **C**. Once again, reaction rates could be improved by carrying out the cyclizations at elevated temperatures (T = 100 °C, t = 30 min). Unfortunately, the diphosphane complex **3** failed to complete the cyclization of 5-hexynoic acid at room or elevated temperatures as degradation of the iridium complex was observed eventually. Although catalyst decomposition was not observed in reactions using **7**, rates were remarkably slow at room temperature and 144 h was needed to complete the reaction.



Scheme 4. The iridium catalyzed intramolecular cyclization of 5-hexynoic acid.

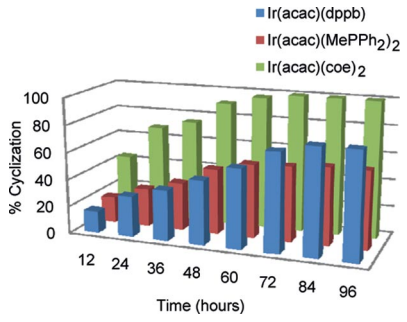


Figure 7. Cyclization of 5-hexynoic acid using iridium complexes **1**, **3**, and **7** at room temperature. Reactions monitored by ^1H NMR spectroscopy and product conversion confirmed by GC/MS.

Conclusions

We have found that complex [Ir(acac)(η^2-coe)$_2$] (**1**) is a moderately stable precursor to a number of different acetylacetonato(phosphane)iridium complexes via addition of monodentate and bidentate phosphanes. Reactions proceed at room temperature to give high yields of the desired square-planar complexes except for those involving dppe, which gave a complicated mixture of products. Complex [Ir(acac)(dppe)] (**5**) was prepared in a microwave reactor at 125 °C. Although all complexes were efficient in the intramolecular catalyzed cyclization of 4-pentynoic acid to give exclusive formation of the exocyclic γ-methylene-γ-butyrolactone, reactions employing complex **1** gave the best rates. Complex **1** could also be used at elevated temperatures to give the desired products in 20 min at 100 °C and was found to be the best precatalyst for the cyclization of 5-hexynoic acid. Further studies will expand the catalytic potential of

these iridium complexes and the scope of these cyclization reactions, and the results of which will be published in due course.

Experimental Section

General: Reagents and solvents were purchased from Aldrich Chemicals and used as received. $[Ir(\mu\text{-}Cl)(\eta^2\text{-coe})_2]_2$[23] and $[Ir(acac)(\eta^2\text{-coe})_2]$ **(1)**[9] were prepared by known procedures. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR (^1H 270 MHz; ^{13}C 68 MHz; ^{31}P 109 MHz) spectrometer. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^1H and ^{13}C) or external H_3PO_4 (^{31}P)] and coupling constants (J) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quintet (quint), multiplet (m), broad (br), and overlapping (ov). Decomposition and melting points were determined using a Mel-Temp apparatus and are uncorrected. A CEM Discover microwave reactor was employed for all microwave reactions and the reaction temperature was monitored by an internal IR pyrometer. Septum sealed, thick-walled reaction tubes were used in order to withstand the elevated pressures inherent with microwave reactions. Elemental analyses were performed by Guelph Chemical Laboratories (Guelph, ON). All reactions were performed under dinitrogen.

Synthesis of $[Ir(acac)(PPh_3)_2]$ (2): Complex **2** was prepared by modification of a known procedure.[7g] To a 5 mL toluene solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (200 mg, 0.39 mmol) was added a 3 mL toluene solution of triphenylphosphane (206 mg, 0.79 mmol). The reaction was allowed to proceed for 18 h at which point an orange-yellow precipitate was collected by suction filtration and washed with cold hexane (1 mL) to afford **2**; yield 300 mg (94%), m.p. 195–199 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^1H δ = 7.84 (m, 12 H, Ar), 6.97–6.87 (ov m, 18 H, Ar), 5.32 [s, 1 H, C(*H*)=C], 1.28 (s, 6 H, CH_3); $^{13}C\{^1H\}$ δ = 181.2 [*C*(O)], 135.8 (m, *C*P), 135.2 (t, J_{CP} = 5.1 Hz, Ar), 128.5 (Ar), 126.8 (t, J_{CP} = 5.1 Hz, Ar), 101.6 [*C*(H)=C], 26.9 (*C*H_3); $^{31}P\{^1H\}$ δ = 19.3. $C_{41}H_{37}IrO_2P_2$ (816.00): calcd. C 60.34, H 4.58; found C 60.61, H 4.85.

$[Ir(acac)(PMePh_2)_2]$ (3): To a 5 mL toluene solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (200 mg, 0.39 mmol) was added a 3 mL toluene solution of methyldiphenylphosphane (156 mg, 0.78 mmol). The reaction was allowed to proceed for 18 h at which point the volume of solvent was reduced by one half under vacuum and the solution stored at –30 °C. The resulting orange-yellow precipitate was collected by suction filtration and washed with cold hexane (1 mL) to afford **3**; yield 225 mg (83%), m.p. 177–180 °C. NMR spectroscopic data (in C_6D_6): ^1H δ = 7.82 (m, 8 H, Ar), 7.08–7.03 (ov m, 12 H, Ar), 5.30 [s, 1 H, C(*H*)=C], 1.71 (d, J_{HP} = 8.4 Hz, 6 H, PCH_3), 1.41 (s, 6 H, acac-CH_3); $^{13}C\{^1H\}$ δ = 181.2 [*C*(O)], 137.9 (m, *C*P), 133.2 (t, J_{CP} = 5.1 Hz, Ar), 128.5 (Ar), 127.2 (t, J_{CP} = 5.1 Hz, Ar), 101.7 [*C*(H)=C], 27.1 (acac-*C*H_3), 16.6 (m, P*C*H_3); $^{31}P\{^1H\}$ δ = –1.6. $C_{31}H_{33}IrO_2P_2$ (691.86): calcd. C 53.81, H 4.82; found C 53.96, H 5.01.

[Ir(acac)(dppm)] (4): To a 5 mL toluene solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (200 mg, 0.39 mmol) was added a 3 mL toluene solution of bis(diphenylphosphanyl)methane (150 mg, 0.39 mmol). The reaction was allowed to proceed for 18 h at which point hexane (5 mL) was added and the solution stored at –30 °C. The resulting orange-yellow precipitate was collected by suction filtration and washed with cold hexane (1 mL) to afford **4**; yield 230 mg (87%), m.p. 95–99 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^1H δ = 8.02 (m, 8 H, Ar), 7.13–6.94 (ov m, 12 H, Ar), 5.44 [s, 1 H, C(*H*)=C], 3.96 (t, J_{HP} = 10.4 Hz, 2 H, PCH_2), 1.73 (s, 6 H, CH_3); $^{13}C\{^1H\}$ δ = 182.0 [*C*(O)], 135.6 (t, J_{CP} = 23.0 Hz, *C*P), 132.4 (t, J_{CP} = 5.6 Hz, Ar), 129.2 (Ar), 127.9 (t, J_{CP} = 4.6 Hz, Ar), 101.7 [*C*(H)=C], 55.3 (t, J_{CP} = 30.2 Hz, P*C*H_2), 27.9 (*C*H_3); $^{31}P\{^1H\}$ δ = –56.5. $C_{30}H_{29}IrO_2P_2$ (675.79): calcd. C 53.32, H 4.33; found C 53.02, H 4.58.

[Ir(acac)(dppe)] (5): To a 5 mL THF solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (200 mg, 0.39 mmol) was added a 5 mL THF solution of 1,2-bis(diphenylphosphanyl)ethane (155 mg, 0.39 mmol). The solution was heated (T = 125 °C) under microwave conditions at 200 W for 1 h. Following removal of solvent the resulting orange solid was washed with hexane (3 × 5 mL) and collected by suction filtration to afford **5**; yield 223 mg (83%), m.p. 142–146 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^1H δ = 8.05 (m, 8 H, Ar), 7.12–7.00 (ov m, 12 H, Ar), 5.39 [s, 1 H, C(*H*)=C], 1.84 (d, J_{HP} = 14.6 Hz, 4 H, PCH_2), 1.64 (s, 6 H, CH_3); $^{13}C\{^1H\}$ δ = 181.7 [*C*(O)], 136.5 (d, J_{CP} = 50.3 Hz, *C*P), 133.1 (t, J_{CP} = 4.6 Hz, Ar), 128.9 (Ar), 127.9 (t, J_{CP} = 4.6 Hz, Ar), 101.7 [*C*(H)=C], 29.6 (m, P*C*H_2), 27.8 (*C*H_3); $^{31}P\{^1H\}$ δ = 33.9. $C_{31}H_{31}IrO_2P_2$ (689.82): calcd. C 53.97, H 4.54; found C 54.16, H 4.88.

[Ir(acac)(dppp)] (6): To a 5 mL toluene solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (200 mg, 0.39 mmol) was added a 3 mL toluene solution of 1,3-bis(diphenylphosphanyl)propane (161 mg, 0.39 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum and the residual solid was triturated with hexane (5 mL) to afford **6** as an orange solid; yield 210 mg (77%), m.p. 97–100 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^1H δ = 7.86 (m, 8 H, Ar), 7.12–7.02 (ov m, 12 H, Ar), 5.24 [s, 1 H, C(*H*)=C], 2.27 (m, 4 H, PCH_2), 1.61 (m, 2 H, PCH_2CH_2), 1.39 (s, 6 H, CH_3); $^{13}C\{^1H\}$ δ = 181.3 [*C*(O)], 136.0 (m, *C*P), 133.7 (t, J_{CP} = 4.6 Hz, Ar), 128.6 (Ar), 127.2 (t, J_{CP} = 4.6 Hz, Ar), 101.4 [*C*(H)=C], 28.4 (m, P*C*H_2), 27.3 (*C*H_3), 20.4 (PCH_2*C*H_2); $^{31}P\{^1H\}$ δ = –0.3. $C_{32}H_{33}IrO_2P_2$ (703.85): calcd. C 54.60, H 4.74; found C 54.91, H 5.05.

[Ir(acac)(dppb)] (7): To a 2 mL toluene solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (125 mg, 0.24 mmol) was added a 3 mL toluene solution of 1,4-bis(diphenylphosphanyl)butane (104 mg, 0.24 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum and the resulting solid was washed with hexane (2 × 1 mL) to afford **7** as an orange solid; yield 150 mg (87%), m.p. 117–120 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^1H δ = 7.84 (m, 8 H, Ar), 7.15–7.10 (ov m, 12 H, Ar), 5.20 [s, 1 H, C(*H*)=C], 2.30 (br. m, 4 H, PCH_2), 1.79 (br. m, 4 H, PCH_2CH_2), 1.34 (s, 6 H, CH_3); $^{13}C\{^1H\}$ δ = 181.0 [*C*(O)], 138.0 (m, *C*P), 133.7 (t, J_{CP} = 4.6 Hz, Ar), 128.5 (Ar), 127.2 (t, J_{CP} = 4.6 Hz, Ar), 101.4 [*C*(H)=C], 29.6 (m, P*C*H_2), 27.1 (*C*H_3), 23.9 (PCH_2*C*H_2); $^{31}P\{^1H\}$ δ = 10.8. $C_{33}H_{35}IrO_2P_2$ (717.88): calcd. C 55.21, H 4.92; found C 55.44, H 5.15.

[Ir(acac)(dppf)] (8): To a 2 mL THF solution of $[Ir(acac)(\eta^2\text{-coe})_2]$ (100 mg, 0.20 mmol) was added a 3 mL THF solution of 1,1′-bis(diphenylphosphanyl)ferrocene (110 mg, 0.20 mmol). The reaction was allowed to proceed for 18 h at which point a yellow precipitate was collected by suction filtration and washed with hexane (2 × 1 mL) to afford **8** as a yellow solid; yield 120 mg (71%), m.p. 215–218 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^1H δ = 8.08 (m, 8 H, Ar), 7.25–7.03 (ov m, 12 H, Ar), 5.17 [s, 1 H, C(*H*)=C], 4.32 (d, J_{HP} = 1.7 Hz, 4 H, Cp), 3.86 (s, 4 H, Cp), 1.29 (s, 6 H, CH_3); $^{13}C\{^1H\}$ δ = 181.3 [*C*(O)], 137.4 (m, PAr), 135.1 (t, J_{CP} = 5.1 Hz, Ar), 128.8 (Ar), 126.9 (t, J_{CP} = 5.1 Hz, Ar), 101.5 [*C*(H)=C], 80.2 (m, PCp), 75.4 (t, J_{CP} = 4.6 Hz, Cp), 71.6 (Cp), 26.9 (*C*H_3); $^{31}P\{^1H\}$ δ = 13.4. $C_{39}H_{35}FeIrO_2P_2$ (845.74): calcd. C 55.38, H 4.18; found C 55.11, H 4.13.

[Ir(acac)(dcpe)] (9): To a 3 mL toluene solution of [Ir(acac)-(η^2-coe)$_2$] (200 mg, 0.39 mmol) was added a 4 mL toluene solution of 1,2-bis(dicyclohexylphosphanyl)ethane (165 mg, 0.39 mmol). The reaction was allowed to proceed for 18 h at which point solvent was removed under vacuum and the resulting solid washed with cold hexane (1 mL) to afford **9** as a yellow solid; yield 200 mg (72%), m.p. 146–150 °C (decomp.). NMR spectroscopic data (in C_6D_6): ^{1}H δ = 5.36 [s, 1 H, C(*H*)=C], 2.46 (br. d, J_{HP} = 12.1 Hz, 4 H, PCH_2), 1.91–1.59 (ov m, 30 H, Cy), 1.69 (s, 6 H, CH_3), 1.29–1.11 (ov m, 14 H, Cy); ^{13}C{^{1}H} δ = 180.1 [*C*(O)], 101.6 [*C*(H)=C], 35.1 (d, J_{CP} = 31.7 Hz, P*C*H), 29.0 (d, J_{CP} = 11.3 Hz, P*C*H$_2$), 28.0 (*C*H$_3$), 27.3 (app t, J_{CP} = 9.7 Hz), 26.7, 24.3 (dd, J_{CP} = 34.8, 8.7 Hz); ^{31}P{^{1}H} δ = 53.7. $C_{31}H_{55}IrO_2P_2$ (714.06): calcd. C 52.14, H 7.78; found C 51.97, H 7.81.

[[Ir(dppe)$_2$]Cl] (10): To a 5 mL toluene solution of [Ir(acac)-(η^2-coe)$_2$] (100 mg, 0.20 mmol) was added a 3 mL toluene solution of 1,2-bis(diphenylphosphanyl)ethane (159 mg, 0.40 mmol) and NBu_4Cl (56 mg, 0.20 mmol). The reaction was allowed to proceed for 18 h at which point an orange solid was collected by suction filtration and washed with cold hexane (1 mL) to afford **10**; yield 75 mg (37%), m.p. 250–256 °C (decomp.). NMR spectroscopic data (in $CDCl_3$): ^{1}H δ = 7.30 (m, 16 H, Ar), 7.24–7.14 (ov m, 24 H, Ar), 2.09 (t, J_{HP} = 9.4 Hz, 8 H, PCH_2); ^{13}C{^{1}H} δ = 133.4 (t, J_{CP} = 2.6 Hz, Ar), 131.2 (Ar), 130.9 (m, *C*P), 128.5 (t, J_{CP} = 2.6 Hz, Ar), 29.6 (app quint, J_{CP} = 12.8 Hz, P*C*H$_2$); ^{31}P{^{1}H} δ = 50.7. $C_{52}H_{48}ClIrP_4{\cdot}0.5C_7H_8$ (1070.95): calcd. C 62.24, H 4.90; found C 62.59, H 4.72.

General Procedure for the Cyclization of Alkynoic Acids: A 0.5 mL CD_3CN solution of alkynoic acid was added to a suspension of the appropriate iridium catalyst (5 mol-%) in 0.5 mL of CD_3CN. The progress of the cyclization was monitored over time by ^{1}H and ^{13}C NMR spectroscopy. Cyclized product NMR spectra were consistent with reported literature values.[22]

X-ray Crystallography: Crystals of **1**, **3**, **4**, and **9** were grown from saturated hexane solutions, at –30 °C, crystals of **10** were grown from a $CDCl_3$ solution layered with hexane at room temp. and crystals of **6** were grown by slow evaporation of a C_6D_6 solution at room temp. Single crystals were coated with Paratone-N oil, mounted using a polyimide MicroMount and frozen in the cold nitrogen stream of the goniometer. A hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. The detector distances were 5 cm. All data collection was performed at 173 K with the exception of **9** which was carried out at 223 K due to loss of crystallinity at lower temperatures. The data were reduced (SAINT)[24] and corrected for absorption (SADABS).[25] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL).[26] The asymmetric cell for **4** contains half a molecule of hexane, which is disordered over multiple sites. This was modelled using disordered electron density (SQUEEZE).[27] The chloroform molecules and chloride anions for **10** were disordered over two positions and refined with site occupancies of 0.5. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and refined using a riding model with the exception of **10** where hydrogen atoms for the chloroform molecules were omitted.

CCDC-774663 (for **1**), -774664 (for **3**), -774665 (for **4**), -774666 (for **10**), -774667 (for **6**), -774668 (for **9**) contain the supplementary crystallographic data for this and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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