

Notes

Catalytic Cyclization of Some Alkynes by Rhodium and Iridium Complexes of Ferrocene-Containing Ligands

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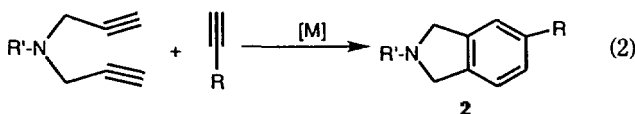
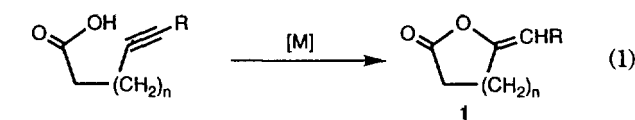
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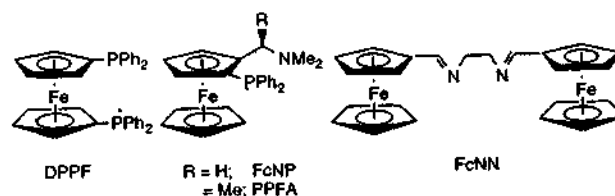
Received July 10, 1995

Interest in the chemistry of exocyclic lactones and exocyclic benzene derivatives such as **1** and **2** has emerged in recent years because of their biological activities¹⁻³ and utility in steroid and alkaloid chemistry.⁴⁻⁶ Due to their ready availability, the catalytic cyclization of α,ω -acetylenic acids and cocyclization of *N*-benzyl-di(propargyl)amine with alkynes as represented in equations 1 and 2, respectively, stand among the most effective approaches to these systems (1 & 2).⁷

Of various catalysts so far employed to affect these reactions,⁸⁻⁹ low-valent groups 8 and 9 metal-phosphine or metal-carbonyl complexes such as [(cyphos)RhCl]₂,¹⁰ (cyphos = 1,2-bis(dicyclohexylphosphino)ethane), (PPh₃)₃RhCl,¹⁰ (PPh₃)₄Pd,¹⁰ CpCo(CO)₂,⁵ and Co₂(CO)₈,⁶ have proven to be the most effective catalysts.



In connection with the rhodium catalysis, we¹¹ have recently reported that the cationic rhodium complexes of the type [(COD)Rh(LL)]ClO₄ and [(LL)RhCl]₂ incorporating chelating bidentate ferrocenyl-phosphines and -imines as ligands (LL) (Scheme 1) are extremely efficient catalysts for the activation of phenylacetylene to give high-molecular-weight polyphenylacetylene (PPA). In that paper it has been demonstrated not only that the presence of the ferrocene ligands is essential for the formation of the high-molecular-weight PPA with high stereoregularity in high yields but that variation of donor sites in the ferrocene moieties are the most crucial reaction parameter. These findings and the facts that both the polymerization of phenylacetylene and the reactions 1 and 2 catalyzed by the rhodium and iridium complexes mentioned above may involve somewhere in the catalytic



Scheme 1.

cycle the same reaction pathways, *i.e.*, initial coordination followed by intramolecular coupling of the acetylenic units, have prompted us to extend further these same catalytic systems to the cyclization reactions in equations 1 and 2 with the hope of the same degree of catalytic efficiency. In this note we present the results of catalytic cyclization represented by equations 1 and 2 employing the ferrocenyl-phosphines and -imine as ligands.

Experimental Section

Reagents and Instruments. All manipulations were conducted under argon or nitrogen atmosphere using a double-manifold vacuum system and Schlenk techniques. All commercial reagents were used as received unless otherwise mentioned. Solvents were purified according to the standard methods.¹² Microanalyses were performed by the Center for Instrumental Analysis, Kyungpook National University. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 300 and 80.15 MHz, respectively. Infrared spectra were recorded on a Ft-IR: Galaxy 6030E, Mattson Instruments. GC-Mass spectra were obtained using a Shimadzu QP-1000 model. GC was performed on a Shimadzu model 15B with FID detector and helium as a carrier gas. 4-Pentynoic acid, *N*-benzyl-di(propargyl)amine, Cp*Rh(CO)₂, [Rh(CO)₂Cl]₂, and Rh₂(OAc)₄ were purchased from Aldrich Chemical Co. and used without further purification. The ligands 1,1'-bis(diphenylphosphino)ferrocene (DPPF),¹³ 2-diphenylphosphino-1-(*N,N*-dimethylaminomethyl)ferrocene (FcNP),¹⁴ 2-diphenylphosphino-1-(*N,N*-dimethylaminoethyl)ferrocene (PPFA),¹⁵ *N,N'*-ethylenebis((ferrocenylmethylidene)amine) (FcNN),¹⁶ and their metal complexes of the types [(COD)M(LL)]ClO₄ (M = Rh, Ir; LL = DPPF, FcNP, FcNN) and [Rh(DPPF)Cl]₂¹⁷ were prepared according to the literature methods.

Synthesis of [(COD)Ir(PPFA)]ClO₄. The title compound was prepared essentially by employing the method for the preparation of [(COD)Rh(LL)]ClO₄. [(COD)IrCl]₂ (256.7 mg, 0.24 mmol) and PPFA (232.9 mg, 0.53 mmol) were placed in a Schlenk tube and toluene (5 mL) was added. To this solution was added a THF (2 mL) solution of NaClO₄ (52.7 mg, 0.53 mmol) with stirring. Orange precipitates formed immediately which was separated on a glass filter and washed with toluene. This was dissolved in a minimum amount of CH₂Cl₂ and a mixture of EtOH and diethyl ether (2/1) was added for crystallization. Red single crystals suitable for X-ray crystallographic studies¹⁸ were grown on cool-

Table 1. Metal-catalyzed lactonization of 4-pentynoic acid^a

Entry	Catalyst	Yield (%) ^b
1	[Rh(DPPF)Cl] ₂	75
2	[(COD)Rh(FcNP)]ClO ₄	60
3	[(COD)Rh(FcNN)]ClO ₄	60
4	[(COD)Rh(DPPF)]ClO ₄	59
5	[(COD)Rh(DPPE)]ClO ₄	40
6	[(COD)Ir(FcNP)]ClO ₄	69
7	[(COD)Ir(FcNN)]ClO ₄	69
8	[(COD)Ir(DPPF)]ClO ₄	40
9	[(CO) ₂ RhCl] ₂	47
10	Cp [*] Rh(CO) ₂	42
11	Rh ₂ (OAc) ₄	20

^aReaction conditions: [catalyst]=2 mol%; solvent=dichloroethane; reaction time=3 h under reflux. ^bGC yield.

ing this solution in a refrigerator. Yield: 87%.

Typical procedure for metal-catalyzed lactonization of alkynoic acid. A flask equipped with a magnetic stirring bar was charged with the catalyst (2-4 mol %) and dichloroethane (20 mL) under the stream of argon. To this was added 4-pentynoic acid (5 mmol) and the resulting solution was refluxed for 3 h. The progress of the reaction was followed by analyzing 1-2 mL aliquots of the solution by GC (OV-17 glass column, 2 m×3.2 m). To determine the GC conversion yield, the response factors of the components were calculated by using a mixture of known amounts of starting material, isolated authentic products, and internal standard (naphthalene).

Typical procedure for metal-catalyzed cocyclization of *N*-benzylpropargylamine with phenylacetylene. A flask was charged with *N*-benzylpropargylamine (1 mmol), phenylacetylene (1.5 mmol), acetonitrile (20 mL), and catalyst (0.01 mol, 1 mol%) under the stream of argon. The reaction mixture was stirred under reflux for 4 h, after which the solution was reduced in volume under reduced pressure to leave an oily residue. This was applied to TLC with a mixture of hexane and ethylacetate (9/1) as an eluent.

Results and Discussion

To determine the effectiveness of the rhodium and iridium complexes prepared in this laboratory as catalysts for the intramolecular lactonization (equation 1), we used 4-pentynoic acid as a standard reagent (R=H; *n*=1). The five-membered exocyclic methylene lactone is known to be the sole product when 4-pentynoic acid is used as the substrate regardless of the catalyst.¹⁰ For comparative purposes, we have also employed other commercially available rhodium complexes. The results are summarized in Table 1.

Of various catalysts employed the dimeric rhodium complex of the type [Rh(DPPF)Cl]₂ gives the highest product yield (75%). The catalytic efficiency of this type of dimeric rhodium species is well established in the literature.¹⁰ This 16-electron dimeric species is likely to undergo chloride bridge cleavage reactions in solution to be in equilibrium with the 14-electron monomer suggested to be an active catalyst.

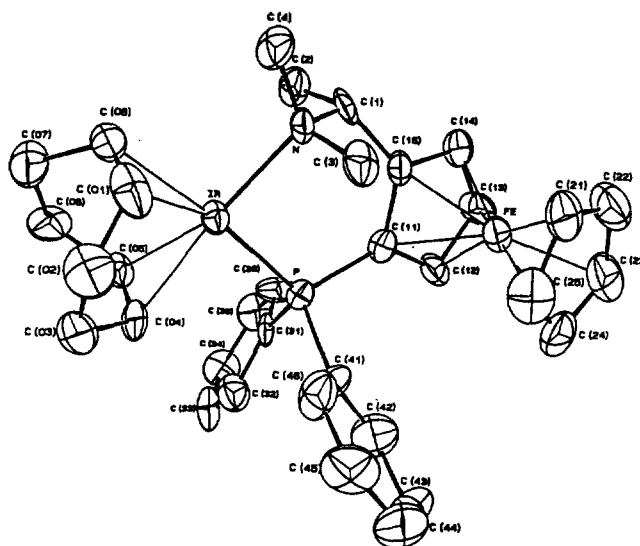
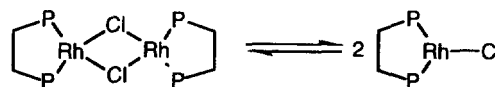


Figure 1. ORTEP diagram of the molecular structure for [(COD)Ir(PPFA)]. Relevant bond distances (Å) and angles (°): Ir-P(1) 2.282(3), Ir-N 2.14(1), Ir-C(01) 2.22(2), Ir-C(08) 2.26(2), Ir-C(04) 2.20(1), Ir-C(05) 2.23(1), N-Ir-P(1) 95.3(3), N-Ir-C(01) 94.3(6), N-Ir-C(08) 93.1(5), N-Ir-C(04) 164.7(4), N-Ir-C(05) 157.4(5), P(1)-Ir-C(01) 150.2(5), P(1)-Ir-C(08) 169.1(4), P(1)-Ir-C(04) 86.7(4), P(1)-Ir-C(05) 91.5(4), C(01)-Ir-C(08) 35.1(6), C(04)-Ir-C(05) 37.0(5), C(01)-Ir-C(04) 77.1(6), C(05)-Ir-C(08) 78.1(5).



Relatively good to moderate product yields (40-70%) were also obtained with cationic rhodium and iridium complexes of the type [(COD)M(LL')]₂ClO₄. Quite interestingly, as for this type of mononuclear complexes, comparison among the ferrocene ligands gives the impression that the presence of at least one nitrogen donor is essential for better yields since the simple chelating diphosphine ligands DPPF and DPPE (=1,2-bis(diphenylphosphino)ethane) give lower yields than their aminophosphine and diimine counterparts such as FcNP and FcNN, respectively (entries 2-5). The same is true with the iridium analogues as can be seen from the table (entries 6-8). The similar observations that the nitrogen-containing ligands FcNP and FcNN serve better than the chelating diphos type ligands such as DPPF in many respects have also been made by us¹¹ with the catalytic polymerization of phenylacetylene. Several attempts have failed to grow single crystals of this type of catalyst containing FcNP and FcNN in order to garner some information about the structure-reactivity relationship. In stead we have succeeded in obtaining the crystal structure of [(COD)Ir(PPFA)]ClO₄, where the ligand PPFA is almost identical with FcNP in that one of the methylene protons in FcNP is replaced with a methyl group. Figure 1 reveals the ligand to form a metallacyclohexene with a chair conformation with iridium. Although the exact role of nitrogen donor on the catalytic activity has yet to be investigated, the unsymmetrical coordination environment around iridium, that is, shorter bond length of Ir-N than that of Ir-P may play a role. Namely

Table 2. Catalytic cocyclotrimerization of *N*-benzylidiz(propargyl)amine with phenylacetylene^a

Entry	Catalyst	Yield (%) ^b
1	[(COD)Rh(DPPF)]ClO ₄	27
2	[(COD)Rh(DPPE)]ClO ₄	15
3	[(COD)Rh(FcNP)]ClO ₄	19
4	Rh(PPh ₃) ₃ Cl	10
5	Cp [*] Rh(CO) ₂	8
6	Co ₂ (CO) ₈	7

^aReaction conditions: [catalyst]=1 mol%; solvent=MeCN; reaction time=4 h under reflux. ^bGC yield.

the more-electronegative nitrogen makes the *trans* Ir-olefin bond makes more labile toward substitution by incoming substrate which in turn undergoes intramolecular cyclization more easily.

As proposed by others,¹⁰ the catalytic cycle may involve an initial oxidative addition of OH of the acid, nucleophilic attack of the carboxylate on the coordinated acetylene followed by reductive elimination to generate the lactone. These same cationic rhodium complexes (Table 1) were found to be poor catalyst, however, when applied to the cocyclotrimerization of *N*-benzylidiz(propargyl)amine with phenylacetylene as presented in equation 2 (R=Ph; R'=benzyl). The results are shown in Table 2. As shown in the table rhodium and cobalt carbonyl complexes which are the well-known catalysts for cyclotrimerization of alkyne derivatives gave even poorer yields in this case.

Acknowledgment. This work was supported by the Ministry of Education (BSRI-94-3403) and KOSEF (94-0501-01).

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- Crystal structure data for (COD)Ir(PPFA)·2CH₃CH₂OH: *a* = 11.008(2), *b* = 11.475(2), *c* = 14.884(3) Å, *b* = 108.19(2)°, *V* = 1784.5(7) Å³, space group P2₁ (No. 4). The single crystals were obtained from ethanol solution. The structure was solved by Patterson method and subsequent difference Fourier techniques and refined by full-matrix least-squares for 473 parameters and 2887 observed reflections (*I* ≥ 3σ(*I*)), *R* = 0.040, *R_w* = 0.044.

Synthesis of Plant Growth Promoting and Fungicidal 4-Quinolinone Metabolites of *Pseudomonas cepacia*

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Received August 4, 1995

A number of 2-alkyl-4-quinolinones have been isolated from both microorganisms and plants, and structurally related *N*-alkyl, *N*-oxide, or *O*-alkyl derivatives have been also found.^{1,2} It was proposed that 2-heptyl-4-quinolinone (5) from a microbial fermentation broth was a condensation product of anthranilic acid and a fatty acid precursor.³ However, biosynthetically different 3-alkyl 4-quinolinones have been isolated in small numbers.⁴⁻⁸ The 4-quinolinone compounds ex-