

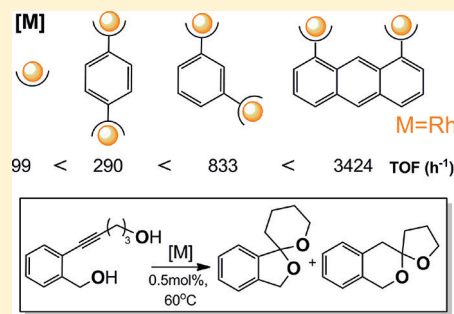
Cooperativity in Bimetallic Dihydroalkoxylation Catalysts Built on Aromatic Scaffolds: Significant Rate Enhancements with a Rigid Anthracene Scaffold

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ABSTRACT: This work describes investigations into metal-catalyzed sequential reactions using a series of single metal and bimetallic Rh(I) and/or Ir(I) pyrazolyl complexes. Monometallic complexes with bis(1-pyrazolyl)methane (bpm) ligands $[M(\text{CO})_2(\text{bpm})]\text{BAR}^F_4$ (**1**), bimetallic complexes $[M_2(\text{CO})_2(L_{\text{scaffold}})]\text{[BAR}^F_4]_2$ (**2–4**) where $M = \text{Rh(I)}$ or Ir(I) bearing bitopic ligands $L_{\text{scaffold}} = \text{bis}(1\text{-pyrazolyl})\text{methane}$ -derived ligands, *p*- $\text{C}_6\text{H}_4[\text{CH}(\text{pz})_2]_2$ (L_{p}), *m*- $\text{C}_6\text{H}_4[\text{CH}(\text{pz})_2]_2$ (L_{m}), and anthracene-bridged $1,8\text{-C}_{14}\text{H}_8[\text{CH}(\text{pz})_2]_2$ (L_{Ant}), $[M_2(\text{CO})_4(L_{\text{p}})]\text{[BAR}^F_4]_2$ (**2**), $[M_2(\text{CO})_4(L_{\text{m}})]\text{[BAR}^F_4]_2$ (**3**), and $[M_2(\text{CO})_4(L_{\text{Ant}})]\text{[BAR}^F_4]_2$ (**4**) were used as catalysts. The efficiency of the complexes as catalysts was tested for the dihydroalkoxylation of a series of alkyne diol substrates, 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (**5**), 1-methyl-3-heptyne-1,7-diol (**6**), 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**7**), and 2-(4-hydroxybut-1-ynyl)benzyl alcohol (**8**), forming spiroketals. All complexes tested were highly effective catalysts for the intramolecular dihydroalkoxylation reaction. The homobimetallic complexes **2–4** showed significant enhancement in activity and selectivity relative to the single metal catalysts (**1**). The order of catalytic activity of the bimetallic complexes was found to be $[M_2(\text{CO})_4(L_{\text{Ant}})]\text{[BAR}^F_4]_2 > [M_2(\text{CO})_4(L_{\text{m}})]\text{[BAR}^F_4]_2 > [M_2(\text{CO})_4(L_{\text{p}})]\text{[BAR}^F_4]_2$ for all substrates, and the bimetallic cooperativity index was established for each reaction.



INTRODUCTION

In recent years there has been increasing focus on the application of bimetallic complexes as homogeneous catalysts,^{1–6} and the highly desired synergistic effect that can occur upon using bimetallic catalysts has been shown in some cases to lead to more effective catalysis. Having two metal centers in close proximity (3.5–6.0 Å) may in some cases lead to enhanced substrate activation or to a more stabilized reaction center.⁷ Thus far, bimetallic catalyst systems have been extensively studied for a number of single-step organic transformations, such as Yuen and Marks' binuclear organo-lanthanide catalyst for hydroamination⁶ and Broussard and co-workers' $[\text{Rh}_2(\text{nbd})_2(\text{et,ph-P}_4)]^{2+}$ active catalyst for hydroformylation.⁵ In 2002, Jones and James investigated the use of Pt/Pd bimetallic complexes as catalysts for a Heck coupling reaction and reported the bimetallic catalyst systems to be more active than the predicted sum of activities of the monometallic "half-unit" analogues. As a result, they proposed a bimetallic cooperativity index (α) as a measure of intermetallic cooperativity between adjacent metal centers in a multimetallic complex with n metal centers.³ Bimetallic "constrained geometry" catalysts consisting of homobimetallic titanium (Ti₂) and zirconium (Zr₂) complexes, as well as a heterobimetallic TiZr complex for ethylene polymerization, have shown that the degree of bimetallic cooperativity between the metal centers in the olefin polymerization reactions is

approximately inversely proportional to the intermetallic distance of the two metal centers.⁸

One-pot tandem reactions allow highly efficient approaches to the synthesis of complex compounds via the formation of several bonds in a single synthetic operation without requiring the isolation of intermediates, addition of reagents, or changing of reaction conditions.⁹ This approach is particularly important in the synthesis of natural products, such as berkelic acid¹⁰ and aspidophytine.¹¹ As a result, transition metal catalyzed one-pot tandem organic transformations have received increasing attention as more efficient and atom-economical approaches to organic heterocycles over traditional multiple single-step reactions.¹² Single metal complexes of Ru(II), Rh(I), and Ir(I) have been previously reported to successfully catalyze tandem reactions of olefin metathesis,¹² hydroformylation,¹² dihydroalkoxylation,^{13,14} and hydroamination/hydrosilylation¹⁵ in good yields and under mild reaction conditions. Multimetallic complexes can also be particularly useful for catalyzing tandem reactions, as multiple metal centers can interact with each other more efficiently for sequential step reactions than monometallic complexes.⁷ Comparably less has been reported of bimetallic catalysts for tandem sequential transformations.¹⁶ One such example has been reported by Peris and co-workers in 2008, where heterobimetallic complexes using triazolyl-diyldine

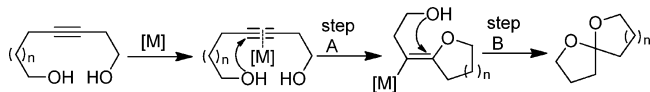
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scaffolds were shown to be highly effective catalysts for a tandem two-step reaction involving the oxidative cyclization of 2-aminophenyl ethyl alcohol, followed by alkylation of the resulting imidazole with a primary alcohol. The Ir^I(COD)/Cp*Ir^{III} bimetallic catalyst system displayed cooperative effects with catalytic activity far exceeding the sum of the individual activities of the Cp*Ir^{III}Cl₂ and Ir^ICl(COD) complexes.¹⁷

The catalyzed one-pot tandem organic transformation approach has been used for the efficient synthesis of spiroketals, biologically active compounds found as components of HIV protease inhibitors,¹⁸ cancer cell inhibitors,¹⁹ and insect sex pheromones.²⁰ Traditional approaches to the synthesis of spiroketals often involve relatively harsh reaction conditions and multiple steps that require further purification.^{21,22} A more direct route to the synthesis of spiroketals is the transition metal catalyzed dihydroalkoxylation of alkyne diols.^{13,14,23} This sequential two-step transformation involves the initial intramolecular hydroalkoxylation of an alkyne to form the first O-heterocycle (step A of Scheme 1), followed by a second

Scheme 1. Tandem Two-Step Dihydroalkoxylation Reaction



cyclization to complete the spiroketal moiety (step B of Scheme 1).¹³ There have been several reports of the metal-catalyzed dihydroalkoxylation reaction, using Rh(I),^{13,14,23} Ir(I),^{13,14,23} Pt(II),²⁴ and Pd(II),^{25,26} complexes as well as Ir(III) hydrides,²⁷ Hg salts,²⁸ and Au(I) and Au(III) halides^{29,30} as catalysts. However the use of bimetallic complexes as catalysts for this two-step dihydroalkoxylation reaction has not yet been reported.

We have previously reported the use of Rh(I) and Ir(I) single metal complexes bearing 1-[2-(diphenylphosphino)ethyl]pyrazole (PyP) and bis(*N*-methylimidazol-2-yl)methane (bim) ligands as catalysts for the dihydroalkoxylation reaction.¹³ More recently we have also shown that Rh(I) and Ir(I) complexes bearing bis(1-pyrazolyl)methane (bpm) ligands, including both monometallic catalysts and dual-metal catalysts where two monometallic complexes are used simultaneously, are highly efficient catalysts for the dihydroalkoxylation of alkyne diols.²³ Significant enhancement of reaction rates was observed in some cases using the dual-metal catalyst systems.²³ We have also recently reported the synthesis of a series of bimetallic Rh(I) and Ir(I) complexes [M₂(CO)₄(L_p)] [BAR^F₄]₂ (2), [M₂(CO)₄(L_m)] [BAR^F₄]₂ (3), and [M₂(CO)₄(L_{Ant})] [BAR^F₄]₂ (4) (Figure 1).³¹ Here we report the catalytic activities of bimetallic complexes 2–4 for the intramolecular dihydroalkoxylation of alkyne diols and investigate the bimetallic cooperativity the complexes display.

RESULTS AND DISCUSSION

Catalyzed Dihydroalkoxylation of Alkyne Diols. The aim of this study was to evaluate the catalytic efficiency of a series of bimetallic complexes (2–4) as catalysts for the dihydroalkoxylation of alkyne diols in the synthesis of spiroketals and establish the degree of bimetallic cooperativity. The Rh(I) and Ir(I) bimetallic catalyst systems, 2–4, as well as their monometallic analogues [M(CO)₂(bpm)]BAR^F₄ (1.1 and 1.2), were assessed for their catalytic activity for the cyclization of a series of alkyne diol substrates (5–8). The reaction

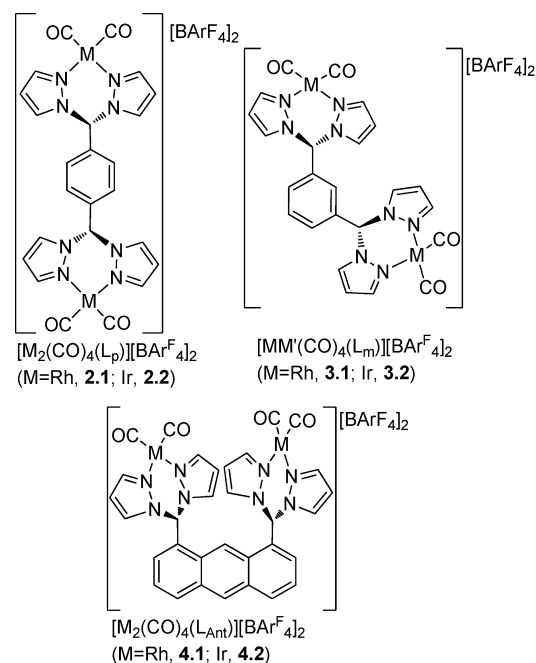


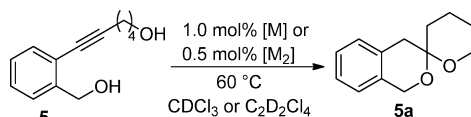
Figure 1. Bimetallic complexes employing binucleating ligands *p*-C₆H₄[CH(pz)₂]₂ (L_p), *m*-C₆H₄[CH(pz)₂]₂ (L_m), and 1,8-C₁₄H₈[CH(pz)₂]₂ (L_{Ant}).

progress was monitored by ¹H NMR spectroscopy at regular intervals, where conversion of substrate to product was determined by integration of the product resonances relative to the substrate resonances in the ¹H NMR spectra. Catalytic efficiency was measured by the TOF (h⁻¹) taken at the point of 50% conversion of substrate to product, as the amount of product formed by one mole of catalyst per hour. The alkyne diol substrates screened included 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (5), 1-methyl-3-heptyne-1,7-diol (6), 2-(5-hydroxypent-1-ynyl)benzyl alcohol (7), and 2-(4-hydroxybut-1-ynyl)benzyl alcohol (8).

According to Baldwin's rules, there is a potential for regioselectivity toward either 5-*exo* or 6-*endo* ring cyclization in the dihydroalkoxylation of alkyne diols such as those used here.³² The rate and regioselectivity of the cyclization can be influenced by several factors including the open-chain structure of the substrate or substituents on the substrate and the size of the ring that is formed. We have previously reported that the efficiency of the ring cyclization as catalyzed by Rh(I) and Ir(I) complexes with bpm ligands was primarily dependent on the ring sizes of the products that are formed. Additionally, the monometallic Ir(I) catalysts with bpm ligands were found to promote 5-*exo* ring cyclization with greater efficiency than their Rh(I) counterparts, while the monometallic Rh(I) catalysts were more effective for the 6-*endo* ring cyclization than the Ir(I) catalysts.²³ We were interested in establishing the effect of bimetallic catalysts for these reactions.

Regioselectivity: Dependence on Metal Center. a. Cyclization of 2-(6-Hydroxyhex-1-ynyl)benzyl Alcohol (5).

The catalyzed double cyclization reaction of the alkyne diol 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (5) using both the monometallic and bimetallic Rh(I) and Ir(I) complexes 1–4 led to the formation of product 5a exclusively, which resulted from two 6-*endo* cyclizations. Each of the catalyzed reactions using the homobimetallic complexes [Rh₂(CO)₄(L_m)] [BAR^F₄]₂ (3.1), [Ir₂(CO)₄(L_m)] [BAR^F₄]₂ (3.2), [Rh₂(CO)₄(L_{Ant})]

Table 1. Catalyzed Tandem Dihydroalkoxylation of Alkyne Diol **5** into the 6,6-Spiroketal Product **5a**^a

catalyst [M] or [M ₂]	time [h] ^b	conv [%]	TOF [h ⁻¹]	catalyst [M] or [M ₂]	time [h] ^b	conv [%]	TOF [h ⁻¹]
[Rh(CO) ₂ (bpm)]BAR ^F ₄ (1.1)	1.59	98	102	[Ir(CO) ₂ (bpm)]BAR ^F ₄ (1.2)	12.67	52	4
[Rh(CO) ₂ (bpm)]BAR ^F ₄ (1.1) ^c	0.59	98	152	[Ir(CO) ₂ (bpm)]BAR ^F ₄ (1.2) ^c	17.63	86	5
[Rh ₂ (CO) ₄ (L _p)]BAR ^F ₄ (2.1) ^c	1.20	98	218	[Ir ₂ (CO) ₄ (L _p)]BAR ^F ₄ (2.2) ^c	23.80	60	6
[Rh ₂ (CO) ₄ (L _m)]BAR ^F ₄ (3.1)	0.47	98	644	[Ir ₂ (CO) ₄ (L _m)]BAR ^F ₄ (3.2)	18.92	68	12
[Rh ₂ (CO) ₄ (L _m)]BAR ^F ₄ (3.1) ^c	0.50	98	480	[Ir ₂ (CO) ₄ (L _{Ant})]BAR ^F ₄ (4.2)	7.28	70	28
[Rh ₂ (CO) ₄ (L _{Ant})]BAR ^F ₄ (4.1)	0.37	98	1012				
[Rh ₂ (CO) ₄ (L _{Ant})]BAR ^F ₄ (4.1) ^c	0.30	98	974				

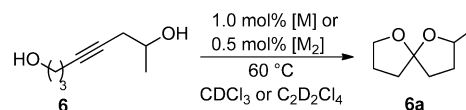
^aDetermined by ¹H NMR spectroscopy. ^bTime taken for product conversion. ^cC₂D₂Cl₄ was used as the solvent instead of CDCl₃.

[BAR^F₄]₂ (**4.1**), and [Ir₂(CO)₄(L_{Ant})]BAR^F₄ (**4.2**) was performed at 60 °C in CDCl₃ for the double cyclization reaction of alkyne diol **5** (Table 1). The catalyzed reactions using the *para*-substituted phenyl complexes [Rh₂(CO)₄(L_p)]BAR^F₄ (**2.1**) and [Ir₂(CO)₄(L_p)]BAR^F₄ (**2.2**) were each carried out with C₂D₂Cl₄ as solvent due to their lack of solubility in CDCl₃ at 60 °C. The catalyzed reactions using complexes **3.1** and **4.1** were also carried out using C₂D₂Cl₄ as solvent so that the efficiencies of the bimetallic complexes can be compared in the different solvents (Table 1).

Overall, the rhodium complexes were found to be superior catalysts compared to their iridium analogues in the formation of the 6,6-spiroketal **5a**, achieving turnover frequencies greater than 100 h⁻¹ and quantitative conversions in less than two hours (Table 1). The same preference was found previously, where Rh(I) complex **1.1** was observed to promote the selective formation of the 6,6-spiroketal **5a** at a greater rate than the Ir(I) analogue **1.2**.²³

For both the rhodium and iridium complexes, the order of activity for the double cyclization of **5** is M₂(L_{Ant}) > M₂(L_m) > M₂(L_p) > M(bpm). All of the bimetallic complexes were more reactive than their monometallic equivalents for the dihydroalkoxylation reaction of **5**. The dirhodium and diiridium complexes where the two metals are held on the anthracene scaffold, M₂(L_{Ant}), were in all cases the best catalyst systems. They are much more active than the corresponding *meta*-phenylene-linked bimetallic complexes, M₂(L_m), which are in turn better than the *para*-phenylene-linked complexes, M₂(L_p) (Table 1).

b. Cyclization of 1-Methyl-3-heptyne-1,7-diol (6). The catalytic activity for the dihydroalkoxylation of the allylic alkyne diol 1-methyl-3-heptyne-1,7-diol (**6**) of the diiridium complexes, **2.2**, **3.2**, and **4.2**, and the most active dirhodium complex, **4.1**, was investigated in CDCl₃ or C₂D₂Cl₄ at 60 °C (Table 2). The reaction proceeded in all cases to exclusively form the 5,5-spiroketal **6a** without any other byproducts. We have previously reported Ir(I) catalysts to be more active than the Rh(I) complexes for promoting the formation of 5,5-spiroketal from the alkyne diol substrates,²³ and therefore only the best Rh(I) catalyst system (**4.1**) was compared here against a series of Ir(I) catalysts. The iridium complexes were confirmed to be superior catalysts over [Rh₂(CO)₄(L_{Ant})]BAR^F₄ (**4.1**). [Ir₂(CO)₄(L_{Ant})]BAR^F₄ (**4.2**) was the best catalyst for the formation of the 5,5-spiroketal (**6a**), where a turnover frequency of 326 h⁻¹ and conversion of 92% in approximately one hour was observed.

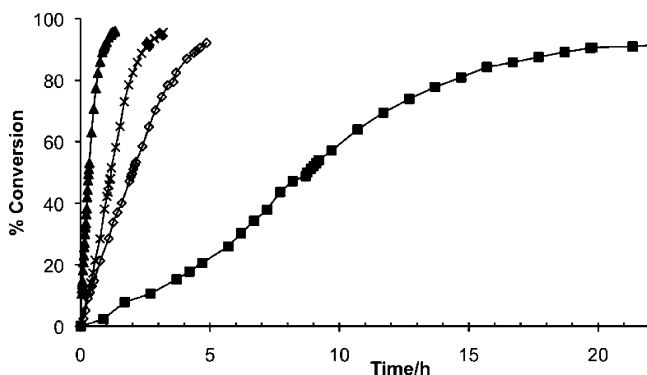
Table 2. Catalyzed Tandem Dihydroalkoxylation of Alkyne Diol **6** into the Nonaromatic 5,5-Spiroketal Product (**6a**)^a

catalyst [M] or [M ₂]	time [h] ^b	conv [%]	TOF [h ⁻¹]
[Rh ₂ (CO) ₄ (L _{Ant})]BAR ^F ₄ (4.1)	16.1	92	48
[Ir(CO) ₂ (bpm)]BAR ^F ₄ (1.2)	4.87	92	25
[Ir ₂ (CO) ₄ (L _p)]BAR ^F ₄ (2.2) ^c	22.5	95	10
[Ir ₂ (CO) ₄ (L _m)]BAR ^F ₄ (3.2)	3.15	95	84
[Ir ₂ (CO) ₄ (L _{Ant})]BAR ^F ₄ (4.2)	1.17	92	326

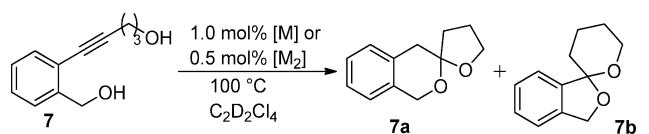
^aDetermined by ¹H NMR spectroscopy. ^bTime taken for product conversion. ^cC₂D₂Cl₄ used as solvent instead of CDCl₃.

For cyclizing alkyne diol **6**, the order of activity of the iridium complexes in terms of TOF is Ir₂(L_{Ant}) > Ir₂(L_m) > Ir(bpm) > Ir(L_p) (Table 2). Chart 1 compares the reaction profiles for

Chart 1. Reaction Profiles of the Iridium-Catalyzed Dihydroalkoxylation of 1-Methyl-3-heptyne-1,7-diol (6) to Give Spiroketal 6a in CDCl₃ at 60 °C with 0.5 mol % [Ir₂(CO)₄(L_{Ant})]BAR^F₄ (4.2**) (▲), [Ir₂(CO)₄(L_m)]BAR^F₄ (**3.2**) (×), [Ir(bpm)(CO)₂]BAR^F₄ (**1.2**) (◇), or [Ir₂(CO)₄(L_p)]BAR^F₄ (**2.2**) (■)**



the iridium complexes, showing the distinct differences between each of the diiridium complexes. [Ir₂(CO)₄(L_{Ant})]BAR^F₄ (**4.2**) exhibits a remarkably enhanced reactivity, with the most rapid initial reaction rate, giving the desired spiroketal in a reaction time of 1.17 h even at a low catalyst loading of 0.5 mol %. Once again, the high reactivity of the *meta*-phenylene and anthracene-bimetallic complexes shows that a bimetallic

Table 3. Catalyzed Tandem Dihydroalkoxylation of Alkyne Diol 7 into the 6,5-Spiroketal (7a) and 5,6-Spiroketal (7b) Products^a


catalyst [M] or [M ₂]	time [h] ^b	conv 7a:7b	TOF [h ⁻¹]	catalyst [M] or [M ₂]	time [h] ^b	conv 7a:7b	TOF [h ⁻¹]
[Rh(CO) ₂ (bpm)]BAR ^F ₄ (1.1)	0.22	1.4:1	961	[Ir(CO) ₂ (bpm)]BAR ^F ₄ (1.2)	0.58	1.1:1	374
[Rh ₂ (CO) ₄ (L _p)] [BAR ^F ₄] ₂ (2.1)	0.10	1.7:1	3174	[Ir ₂ (CO) ₄ (L _p)] [BAR ^F ₄] ₂ (2.2)	0.70	1.4:1	826
[Rh ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.1)	0.06	1.4:1	5988	[Ir ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.2)	0.55	1.4:1	1092
[Rh ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.1)	0.08	1.3:1	9523	[Ir ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.2)	0.27	1.7:1	2468

^aDetermined by ¹H NMR spectroscopy. ^bTime taken to reach >98% conversion of substrate to 7a and 7b.

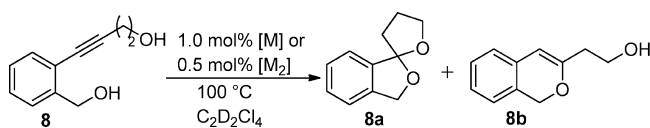
cooperative pathway is likely to exist in the catalyzed dihydroalkoxylation reaction.

Formation of Spiroketal with Mixed Ring Sizes. The catalyzed dihydroalkoxylation reactions of alkyne diols 7 and 8 were carried out in C₂D₂Cl₄ at 100 °C, each leading to two products of different ring sizes (Tables 3 and 5). These

Table 4. Conversion of Alkyne Diol 7 to Form 7a and 7b with Variation in Both Temperature and Catalyst Loading Using [Rh₂(CO)₄(L_m)] [BAR^F₄]₂ (3.1) and [Rh₂(CO)₄(L_{Ant})] [BAR^F₄]₂ (4.1)^a

catalyst [M ₂]	temp [°C]	[M ₂] mol %	time [h] ^b	conv 7a:7b	TOF [h ⁻¹]
[Rh ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.1) ^c	25	0.50	2.42	0.5:1	72
[Rh ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.1)	60	0.50	0.16	0.8:1	3424
[Rh ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.1) ^d	100	0.50	0.08	0.8:1	9522
[Rh ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.1)	100	0.50	0.06	1.4:1	5988
[Rh ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.1)	100	0.25	0.09	1.3:1	8334
[Rh ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.1)	100	0.10	0.24	1.3:1	13 812

^aDetermined by ¹H NMR spectroscopy. C₂D₂Cl₄ used as solvent unless stated otherwise. ^bTime taken to reach >98% conversion of substrate to 7a and 7b. ^cCD₂Cl₂ used as solvent. ^d97% conversion.

Table 5. Catalyzed Tandem Dihydroalkoxylation of Alkyne Diol 8 into the 5,5-Spiroketal Product (8a) and Monocyclized Product (8b)^a

catalyst [M] or [M ₂]	time [h] ^b	conv 8a:8b	TOF [h ⁻¹]
[Rh(CO) ₂ (bpm)]BAR ^F ₄ (1.1)	0.09	1.8:1	1121
[Rh ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.1)	0.18	1.5:1	2008
[Rh ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.1)	<0.03 ^c	2.3:1	>3030
[Ir(CO) ₂ (bpm)]BAR ^F ₄ (1.2)	0.42	3.6:1	535
[Ir ₂ (CO) ₄ (L _p)] [BAR ^F ₄] ₂ (2.2)	0.33	6.2:1	2066
[Ir ₂ (CO) ₄ (L _m)] [BAR ^F ₄] ₂ (3.2)	0.23	6.4:1	2408
[Ir ₂ (CO) ₄ (L _{Ant})] [BAR ^F ₄] ₂ (4.2)	0.14	14.7:1	2754

^aDetermined by ¹H NMR spectroscopy. ^bTime taken to reach >98% conversion of substrate to 8a and 8b. ^cReaction completed in less than 1.8 min.

reactions proceeded notably faster than the dihydroalkoxylation reactions of alkyne diols 5 and 6, which exclusively form single products of a single ring size.

Cyclization of 2-(5-Hydroxypent-1-ynyl)benzyl Alcohol (7) Yielding Both 5,6- and 6,5-Spiroketal. The efficiency of the homobimetallic complexes as catalysts for the cyclization of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (7) to produce the mixed 5,6- and 6,5-spiroketal (7a and 7b) was also investigated using 0.50 mol % of the respective homobimetallic complexes in C₂D₂Cl₄ at 100 °C (Table 3). All of the homobimetallic complexes were found to be much more active than their respective monometallic analogues in promoting the cyclization of 7. Of note is the change in regioselectivity from the monometallic to the bimetallic catalyzed reaction, where increased formation of 7a over 7b was observed in the presence of the bimetallic complexes. In terms of bimetallic reactivity, the anthracene-linked bimetallic complexes (4.1 and 4.2) were again more effective than the *meta*-phenylene complexes (3.1 and 3.2), while the *para*-phenylene analogues (2.1 and 2.2) were the least efficient bimetallic catalysts. This order of bimetallic reactivity corresponds to the order of reactivity for the catalyzed cyclization of alkyne diols (5 and 6) described above. The Rh(I) complexes were consistently superior catalysts to their Ir(I) analogues for this cyclization.

To establish the dependence of the catalyst efficiency on catalyst loading, the catalyst loading of the dirhodium complex [Rh₂(CO)₄(L_m)] [BAR^F₄]₂ (3.1) was varied from 0.50 mol % to 0.25 mol % and 0.10 mol % (Table 4). No significant decrease in reaction time was observed on decreasing the catalyst loading. Indeed, the use of 0.10 mol % [Rh₂(CO)₄(L_m)] [BAR^F₄]₂ (3.1) for the catalyzed cyclization of 7 leads to quantitative (>98%) conversion of the spiroketal products 7a and 7b in 0.24 h, with a turnover frequency at 50% conversion of 13 812 h⁻¹ (Table 4). Although the initial reaction rate was consistently higher with lower catalyst loading, the reaction time for complete conversion increased slightly at the lowest loading used. This suggests that this is the lower limit for improving the effective catalyst loading. The temperature dependence of the catalysis was established for [Rh₂(CO)₄(L_{Ant})] [BAR^F₄]₂ (4.1) for the dihydroalkoxylation of 7 (Table 4). As expected, changing the temperature from 100 °C to 60 °C and 25 °C led to an increase in substrate conversion times (0.08 h to 0.16 h to 2.42 h) and a decrease in turnover frequencies (9522 h⁻¹ to 3424 h⁻¹ to 72 h⁻¹). Remarkably, the double cyclization reaction of 7 proceeds well using 0.50 mol % of [Rh₂(CO)₄(L_{Ant})] [BAR^F₄]₂ (4.1) at room temperature, with quantitative conversion in 2.42 h.

b. Cyclization of 2-(4-Hydroxybut-1-ynyl)benzyl Alcohol (8). The catalyzed reaction of alkyne diol 2-(4-hydroxybut-1-ynyl)benzyl alcohol **8** was carried out in $C_2D_2Cl_4$ at 100 °C to give a mixture of the double-cyclized 5,5-spiroketal (**8a**) and monocyclized pyran (**8b**) products. Both rhodium and iridium complexes were found to be highly efficient catalysts for this reaction, with all catalysts achieving quantitative conversion in less than half an hour (Table 5). Rhodium catalysts were faster than iridium catalysts in carrying out the overall reaction, with dirhodium catalyst **4.1** being the most efficient, achieving a turnover frequency greater than 3030 h^{-1} . However, significantly higher selectivity for 5-*exo* cyclization is observed for the iridium-catalyzed systems, in particular for complex **4.2**, where a product conversion ratio of **8a**:**8b** = 14.7:1 was obtained. This provides another example where Ir(I) catalysts are more efficient at promoting 5-*exo* cyclization than Rh(I) catalysts. The efficiency of the Ir(I) catalysts for the double cyclization to form **8a** notably decreases in the order $Ir_2(L_{Ant}) > Ir_2(L_M) > Ir_2(L_P) > Ir(bpm)$.

Single- versus Dual- Catalyst Systems. We have previously reported a dual Rh(I)/Ir(I) monometallic catalyst system that is highly efficient for the dihydroalkoxylation of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**7**).²³ The dual catalyst system combining monometallic Rh(I) (**1.1**) and Ir(I) (**1.2**) complexes was found to proceed at a rate approximately 17 times greater than the single Rh(I) (**1.1**) catalyst system at equivalent metal catalyst loading (Table 6). The dual Rh(I)/

Table 6. Catalyzed Tandem Dihydroalkoxylation of Alkyne Diol **7 Using a Series of Monometallic and Bimetallic Complexes^a**

catalyst [M]	[M] mol %	time [h] ^b	conv 7a:7b	TOF [h ⁻¹]
$[Rh(CO)_2(bpm)]BAR^F_4$ (1.1)	1.0	0.22	1.4:1	961
$[Rh(CO)_2(bpm)]BAR^F_4$ (1.1) + $[Ir(CO)_2(bpm)]BAR^F_4$ (1.2) ^c	0.50 + 0.50	0.13	0.8:1	1694
$[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.1) + $[Ir_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.2)	0.25 + 0.25	0.23	0.6:1	5208
$[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.1)	0.50	0.08	1.3:1	9523

^aDetermined by ¹H NMR spectroscopy using 1 mol % catalyst in $C_2D_2Cl_4$ at 100 °C. ^bTime taken to reach >98% conversion of substrate to **7a** and **7b**. ^cAs previously reported.²³

Ir(I) catalyst was found to work cooperatively to promote a highly efficient dual activation pathway for both the 5-*exo* and 6-*endo* ring cyclization in the dihydroalkoxylation of alkyne diols.²³ Here a series of dual bimetallic catalyst systems were screened against single-metal catalyst systems to test the effect of varying metal centers and investigate the use of “dual” bimetallic complexes. These reactions were carried out using a total metal catalyst loading of 1 mol % in $C_2D_2Cl_4$ at 100 °C (Table 6).

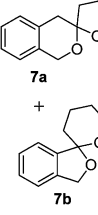


The dual bimetallic catalyst system $\{[Rh_2(L_{Ant})] (\mathbf{4.1}) + [Ir_2(L_{Ant})] (\mathbf{4.2})\}$ was more efficient in terms of initial TOF than either dual monometallic or single monometallic catalysts (Table 6). More surprisingly, however, is that the single bimetallic catalyst system of $[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ was found to be the most efficient catalyst, more efficient than the dual bimetallic catalyst system of $\{[Rh_2(L_{Ant})] (\mathbf{4.1}) + [Ir_2(L_{Ant})] (\mathbf{4.2})\}$. The single $[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ -catalyzed system achieved quantitative conversion of alkyne

diol **7** in less than five minutes with a TOF of 9523 h^{-1} (Table 6). This suggests that for bimetallic catalyst systems the catalytic efficiency for the dihydroalkoxylation of **7** is enhanced to a greater degree by the cooperativity within the bimetallic complex than is achieved by the cooperativity between the two different metal complexes of the dual catalyst system.

Bimetallic Cooperativity: Dependence of Catalytic Efficiency on Scaffold Structure. The bimetallic catalyst systems used here are highly efficient and more importantly demonstrate enhanced catalytic activity compared to their monometallic analogues. This indicates that the presence of a second metal in the bimetallic catalyst system produces a synergistic or cooperative effect between adjacent metal centers, which is absent in a monometallic catalyst system of equivalent metal catalyst loading.

The cooperativity index (α), previously proposed by Jones and James, was used in this work to gauge the degree of intermetallic cooperativity of the bimetallic catalyst systems (Table 7).³ The cooperativity index α was calculated using eq 1,

Table 7. Bimetallic Cooperativity Indices for the Catalyzed Dihydroalkoxylation of Alkyne Diols **5, **6**, and **7** at 60 °C in $C_2D_2Cl_4$ unless Otherwise Noted^a**

Product	Catalyst [M] or [M ₂]	TOF [h ⁻¹]	Coop. Index (α) ^b
	$[Rh(CO)_2(bpm)]BAR^F_4$ (1.1)	99	-
	$[Rh_2(CO)_4(L_P)][BAR^F_4]_2$ (2.1)	290	0.9
	$[Rh_2(CO)_4(L_m)][BAR^F_4]_2$ (3.1)	833	6.4
	$[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.1)	3424	32.6
	$[Ir(CO)_2(bpm)]BAR^F_4$ (1.2)	13	-
	$[Ir_2(CO)_4(L_P)][BAR^F_4]_2$ (2.2)	8	-1.3
	$[Ir_2(CO)_4(L_m)][BAR^F_4]_2$ (3.2)	22	-0.3
	$[Ir_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.2)	190	12.6
	$[Rh(CO)_2(bpm)]BAR^F_4$ (1.1) ^c	102	-
	$[Rh(CO)_2(bpm)]BAR^F_4$ (1.1)	152	-
	$[Rh_2(CO)_4(L_P)][BAR^F_4]_2$ (2.1)	218	-0.5
	$[Rh_2(CO)_4(L_m)][BAR^F_4]_2$ (3.1) ^c	644	4.3
	$[Rh_2(CO)_4(L_m)][BAR^F_4]_2$ (3.1)	480	1.1
	$[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.1) ^c	1012	7.9
	$[Rh_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.1)	974	4.4
	$[Ir(CO)_2(bpm)]BAR^F_4$ (1.2) ^c	25	-
	$[Ir_2(CO)_4(L_P)][BAR^F_4]_2$ (2.2) ^c	10	-1.6
	$[Ir_2(CO)_4(L_m)][BAR^F_4]_2$ (3.2) ^c	84	1.3
	$[Ir_2(CO)_4(L_{Ant})][BAR^F_4]_2$ (4.2) ^c	326	11.0

^aDetermined by ¹H NMR spectroscopy. ^bThe index of cooperativity was determined using eq 1. ^c $CDCl_3$ used as solvent.

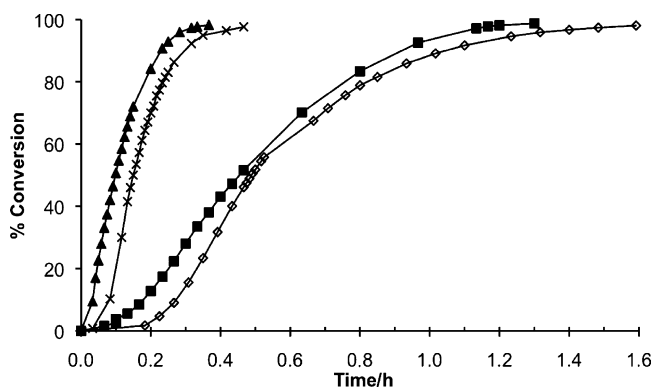
where A_0 is taken as the TOF values at 50% conversion of substrate to products of the bimetallic catalyst system, and A_P as the predicted total TOF value at 50% conversion of substrate to products of the multimetallic catalyst with n metal centers (eq 2). For the bimetallic cooperativity index α to be applicable, it is assumed that the reaction being considered is first order. Although the kinetics of the catalyzed dihydroalkoxylation

reaction discussed here is not known, pseudo-first-order kinetics has been assumed in the first instance (Chart 2).

$$\alpha = \frac{A_0 - A_p}{\bar{A}} \quad (1)$$

$$A_p = \sum_i^n A_i \quad (2)$$

Chart 2. Reaction Profile for Rhodium-Catalyzed Tandem Dihydroalkoxylation of Alkyne Diol 5 into the 6,6-Spiroketal Product 5a, in CDCl₃ at 60 °C with 0.5 mol % [Rh₂(CO)₄(L_{Ant})] [BAR^F₄]₂, 4.1 (▲), [Rh₂(CO)₄(L_m)] [BAR^F₄]₂, 3.1 (×), [Rh₂(CO)₄(L_p)] [BAR^F₄]₂, 2.1 (■), or [Rh(bpm)(CO)₂][BAR^F₄]₂, 1.1 (◇)

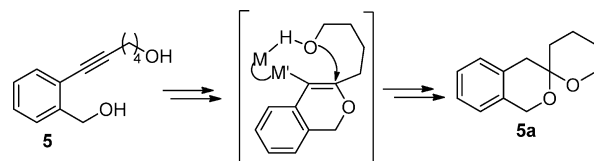


A consistent increase in the bimetallic cooperativity based on scaffold structure, $M_2(L_p) < M_2(L_m) < M_2(L_{Ant})$, was observed for all of the catalyzed dihydroalkoxylation reactions studied (Table 7). This phenomenon may be attributed to differences in structure of the bimetallic catalyst systems. The bimetallic complex [Ir₂(CO)₄(L_p)] [BAR^F₄]₂ (2.2) consistently shows the lowest bimetallic cooperativity with the iridium centers on opposite ends of the phenyl scaffold. The negative α value obtained for this diiridium catalyst (2.2) suggests that its *para*-structure instigates a negative cooperative effect, which slows the catalyzed tandem dihydroalkoxylation reaction (Table 7). On the other hand, the more catalytically active [Rh₂(CO)₄(L_{Ant})] [BAR^F₄]₂ (4.1) complex with consistently the highest cooperativity index has the two rhodium centers on the same side of the anthracene scaffold and close together in space. As this species obtained the highest α value of 32.6, this suggests that having the adjacent metal centers in close proximity to each other enhances intermetallic cooperativity.

Mechanism. We have previously proposed a mechanism for the catalyzed intermolecular dihydroalkoxylation of 4-pentyn-1-ol with methanol.^{13,33} NMR studies indicated the cycle is initiated by π -coordination of the metal complex to the alkyne, followed by nucleophilic attack of the hydroxy group at the alkyne carbon with the greater carbocation character.¹³ Recent DFT studies on the mechanism for the Ir(I) intermolecular catalyzed dihydroalkoxylation of 4-pentyn-1-ol with methanol indicated that hydrogen bonding between the alkyne and methanol serves to stabilize the positive charge that develops at the hydroxyl proton upon ring closure.³³ In the case of the intramolecular catalyzed dihydroalkoxylation of an alkyne

diol, the presence of an adjacent metal center in a bimetallic catalyst system may play a similar role to that of methanol for the intermolecular cyclization. Thus the close proximity of a second metal center may influence the reactivity of both the initial and second cyclization steps. In this model, the unbound metal center orientates and stabilizes the key reaction intermediates through interactions with the second hydroxyl group (e.g., Scheme 2, for the second cyclization step). Such an

Scheme 2. Proposed Key Intermediate for the Bimetallic Catalyzed Intramolecular Dihydroalkoxylation of an Alkyne Diol



intermediate could then facilitate rapid intramolecular addition to the metal-bound alkene. Similarly in the initial step of the reaction cycle one of the two metal centers could associate with the alkyne triple bond, with the second metal weakly interacting with the first hydroxyl group. As a result, the cooperative effects of having two metal centers in close proximity can help accelerate the cyclization steps and achieve greater efficiencies for the dihydroalkoxylation reaction. A further possibility is that the alkyne could coordinate initially to both metal centers, making it more susceptible to nucleophilic attack by the OH group than would be the case with coordination to a single metal center.

SUMMARY AND CONCLUSIONS

Homobimetallic dirhodium(I) and diiridium(I) complexes [M₂(CO)₄(L_{Ant})] [BAR^F₄]₂ (4.1, 4.2) [M₂(CO)₄(L_m)] [BAR^F₄]₂ (3.1, 3.2), and [M₂(CO)₄(L_p)] [BAR^F₄]₂ (2.1, 2.2) were investigated as catalysts for the intramolecular dihydroalkoxylation of a series of alkyne diol substrates, 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (5), 1-methyl-3-heptyne-1,7-diol (6), 2-(5-hydroxypent-1-ynyl)benzyl alcohol (7), and 2-(4-hydroxybut-1-ynyl)benzyl alcohol (8), forming a series of 5,5-, 6,6-, 5,6-, and 6,5-spiroketal units.

In the formation of the 6,6-spiroketal, the dirhodium complexes were more effective as catalysts for the cyclization of 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (5) than their diiridium analogues. On the other hand, the diiridium complexes were found to be more active in cyclizing 1-methyl-3-heptyne-1,7-diol (6) and 2-(4-hydroxybut-1-ynyl)benzyl alcohol (8) to produce 5,5-spiroketal.

In comparison to the single metal catalysts, the homobimetallic catalyst systems showed significantly enhanced activity and selectivity. The order of bimetallic reactivity was $M_2(L_{Ant}) > M_2(L_m) > M_2(L_p)$, where the anthracene-linked complexes were observed to be the best catalysts in all of the dihydroalkoxylation reactions. The enhancement observed was attributed to cooperativity between the metal pairs, and a bimetallic intermediate for the reaction pathway is proposed. The dual bimetallic catalysts did not provide any greater reactivity enhancement than the most effective single bimetallic system.

The degree of intermetallic cooperativity was established using an intermetallic cooperativity index. This indicated that

the degree of bimetallic cooperativity followed the same trend as the relative catalytic efficiency, with $M_2(L_{\text{Ant}}) > M_2(L_m) > M_2(L_p)$ in all cases. Where the complexes with the anthracene scaffolds displayed significant levels of cooperativity between metals, the complexes with the two complexes located *para* on the phenylene backbone typically showed negative cooperativity. This indicates that although enhancement of catalyst activity through bimetallic interactions was observed for the complexes with the ligand pairs bound to the anthracene scaffold, this was not the case for the complexes with the ligands disposed *para* on the phenylene scaffold. Studies of the relative stabilities of the three-dimensional structures of the bimetallic systems are underway.

EXPERIMENTAL SECTION

2-(6-Hydroxyhex-1-ynyl)benzyl alcohol (**5**),¹³ 1-methyl-3-heptyne-1,7-diol (**6**),¹³ 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**7**),¹³ 2-(4-hydroxybut-1-ynyl)benzyl alcohol (**8**),¹³ $[\text{Rh}(\text{CO})_2(\text{bpm})][\text{BAR}^F_4]$ (**1.1**),³⁴ $[\text{Rh}_2(\text{CO})_4(L_p)][\text{BAR}^F_4]_2$ (**2.1**),³¹ $[\text{Rh}_2(\text{CO})_4(L_m)][\text{BAR}^F_4]_2$ (**3.1**),³¹ $[\text{Rh}_2(\text{CO})_4(L_{\text{Ant}})][\text{BAR}^F_4]_2$ (**4.1**),³¹ $[\text{Ir}(\text{CO})_2(\text{bpm})][\text{BAR}^F_4]$ (**1.2**),³⁴ $[\text{Ir}_2(\text{CO})_4(L_p)][\text{BAR}^F_4]_2$ (**2.2**),³¹ $[\text{Ir}_2(\text{CO})_4(L_m)][\text{BAR}^F_4]_2$ (**3.2**),³¹ and $[\text{Ir}_2(\text{CO})_4(L_{\text{Ant}})][\text{BAR}^F_4]_2$ (**4.2**)³¹ were prepared according to literature procedures. On cyclization of each of the alkyne diol substrates, 2-(6-hydroxyhex-1-ynyl)benzyl alcohol (**5**), 1-methyl-3-heptyne-1,7-diol (**6**), 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**7**), 2-(4-hydroxybut-1-ynyl)benzyl alcohol (**8**), and the 5,5-, 6,6-, 5,6-, and 6,5-spiroketal units **5a**,²³ **6a**,^{23,35} **7a** and **7b**,^{13,36} **8a**,^{13,36,37} and **8b**^{13,36a} were formed, respectively.

Thermal-catalyzed dihydroalkoxylation reactions were conducted in NMR tubes fitted with concentric Teflon (Youngs) valves under an inert atmosphere. The catalytic reactions were performed within the NMR spectrometer or in an oil bath if prolonged heating was required. The temperature in the NMR magnet was calibrated using an Omega microprocessor thermometer (model HH23) or neat ethylene glycol. The reaction progress was monitored by ¹H NMR spectroscopy at regular intervals. Characterization of products was confirmed by literature data. The conversion of substrate to product was determined by integration of the product resonances relative to the substrate resonances in the ¹H NMR spectra. The TOF (h⁻¹) taken at the point of 50% conversion of substrate to product was calculated as the amount of product formed by one mole of catalyst per hour.

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