Cyclometallated Ir(III), Rh(III) and Ru(II) complexes as catalysts for the cyclotrimerisation of 1,6-diynes with monoynes

Ronald Grigg,[a*1] Colin Kilner,[a] Meena Senthilnanthanan,[a] Ché R. Seabourne,[a] Visuvanathar Sridharan,[a] and Barry A. Murrer[b]

[a] *Molecular Innovation, Diversity and Automated Synthesis (MIDAS) Centre, School of Chemistry, The University of Leeds, Leeds LS2 9JT*
[b] *Johnson Matthey, Blounts Court, Sonning Common, Reading RG4 9NH*
E-mail: r.grigg@leeds.ac.uk

Abstract
A new series of Rh, Ir and Ru precatalysts for the [2+2+2] cyclotrimerisation of 1,6-diynes with monoynes is reported. The precatalysts are reduced in situ to the active catalysts by reduction with alcohols. The precatalysts activity is in the order Ru>Rh>Ir which reflects the ease of this reduction. The Rh and Ir precatalysts require temperature in excess of 140 ^{o}C allowing their preparation in 2-methoxymethanol at 125 ^{o}C. The mechanism of this process is discussed.

Keywords: Cyclometallated complexes, cyclotrimerisation, diynes, precatalysts

Introduction

The exploitation of cyclometallated complexes in catalysis has recently evolved as a broad new strategy. A variety of palladacycles incorporating cyclometallated phosphines,[1] phosphites,[2] carbenes,[3] imines,[4] heterocycles,[5] thioethers,[6] and oximes[7] have been reported to catalyse carbon-carbon (Heck, Suzuki) and carbon-nitrogen bond forming processes with high turnover numbers.[8,9] Additionally, chiral palladacycles have been shown to catalyse carbon-carbon bond forming processes such as the aldol reaction,[10] Michael addition[11] and cyclopropanation reactions[12] with high enantiomeric excesses. Studies on the synthesis and catalytic behaviour of orthometallated complexes of Rh(II)[13], Rh(III)[14], Ir(I)[15] , and Ru(II)[16] have revealed active catalysts of high efficiency. For example, Nishiyama *et al.* reported that the chiral orthometallated rhodium (III) complex **1** effects the catalytic enantioselective allylation of aldehydes.[17] Other useful applications of the cyclometallated transition metal complexes include electroluminescent/photoluminescent devices[18] and antibacterial agents.[19]

[1] Ron Grigg was Chairman of the RSC Heterocyclic Group during the period 1983-1985.

Results and Discussion

In this paper we report the synthesis of cyclometallated Rh(III), Ir(III) and Ru(II) complexes and their application as precatalysts for cyclotrimerisation of 1,6-diynes with monoynes. These were postulated as potential precatalysts that upon *in situ* reduction would liberate coordinatively unsaturated non-phosphine ligated M(I)/M(0) catalysts. Initally we explored the synthesis of ortho-metallated complexes of Rh(III) and Ir(III) with *N*-phenylpyrazole as the ligand (for the first generation catalysts) employing the protocol used by Nonoyama for their synthesis.[20] Thus the corresponding transition metal chloride and *N*-phenylpyrazole in 2-methoxyethanol under reflux afforded the dimeric complexes **2a,b** in 55-65% yield. Attempts to prepare cycloruthenated complexes by the same method failed, yielding a black powdery substance believed to Ru black. Hence, the ortho-metallated ruthenium(II) complex **4** was prepared in 61% yield by transmetallation of the corresponding mercury(II) complex **3** with $[Ru(p\text{-cymene})Cl_2]_2$ in acetonitrile at room temperature (Scheme1)[21] or stirring $[Ru(p\text{-cymene})Cl_2]_2$ and *N*-phenyl pyrazole in the presence of sodium acetate in DCM at room temperature which afford **4** in 73% yield Confirmation of the structure of **4** was provided by X-ray crystallography (Figure 1).

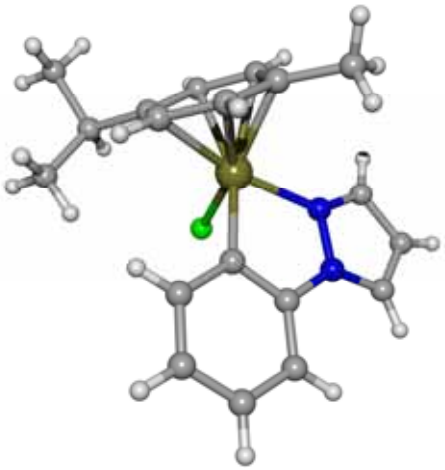
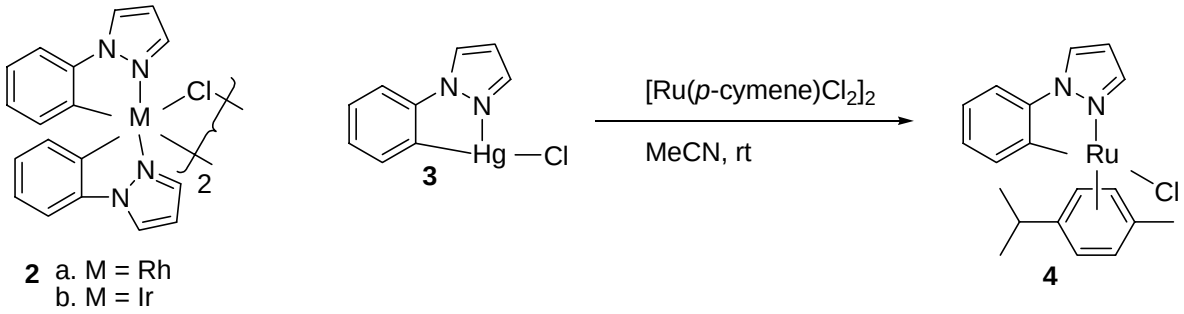


Figure 1



Sheme 1

Next we varied the electronic/steric properties of the ligands employing 2-phenylbenzothiazole, *N*- (*m*-methoxyphenyl)pyrazole, and 3,5-dimethyl-2-phenylpyrazole as ligands in the preparation of cyclometallated complexes **5** and **6** as second generation precatalysts. Dimeric cyclometallated complexes **5a,b** were obtained in 77-86% yield. Complex **6** was obtained in 45% yield and its X-ray crystal structure established that it was a monomer (Figure 2). Steric hindrance of the methyl groups on the pyrazole ring of the ligand prevent formation of the dimeric Rh(III) complex.

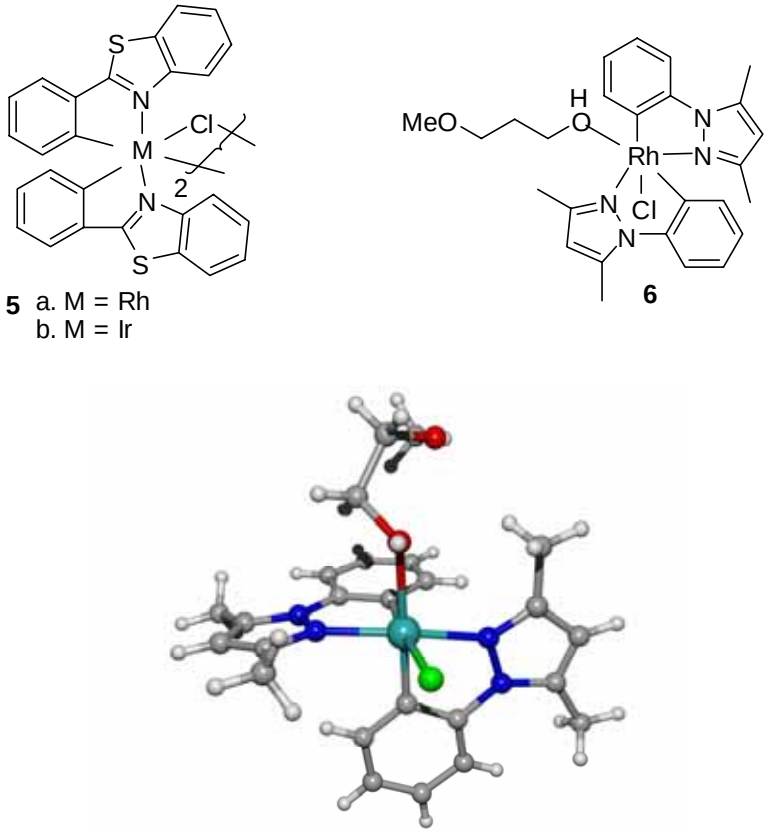
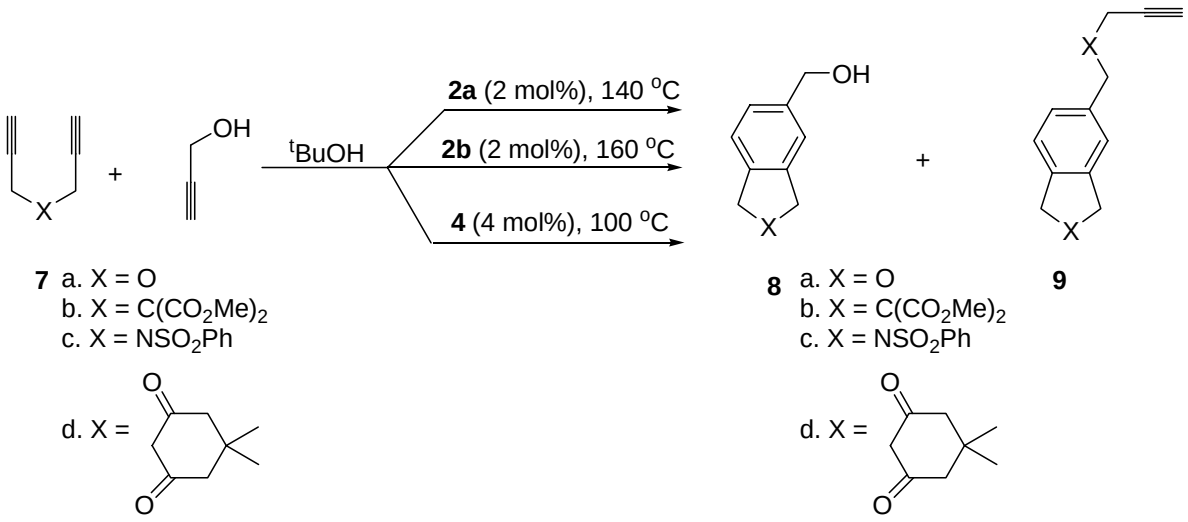


Figure 2

The metal catalysed [2+2+2]-cycloaddition reactions of alkynes is one of the most direct methods to generate polysubstituted benzenes, pyridines and annelated benzene derivatives. Early studies involved the use of a stoichiometric amount of the cobalt(0) complex, $C_pCo(CO)_2$, to promote the cyclotrimerisation.[22] A wide variety of functional groups such as alkyl, aryl, vinyl, CH_2OH, CO_2R, NR_2, SR, SiR_3 , $B(OR)_2$, Br and I are tolerated in the process.[23,24] We reported that a catalytic amount of Wilkinson's catalyst, $RhCl(PPh_3)_3$ effects [2+2+2]-cycloadditions analogous to those promoted by stoichiometric amounts of the $C_pCo(CO)_2$ complex.[25] Since then various other transition metal catalysts based on Ni, Co, Pd, Cr, Rh, Fe, Zr, Nb, and Ir have been developed for alkyne trimerisation reactions.[26] Cyclometallated

complexes of Rh(III), Ir(III) and Ru(II) have not, to our knowledge, been reported as precatalysts for the [2+2+2]-cycloaddition of alkynes. This encouraged us to evaluate complexes **2-6** for such reactions.

Initally, the 1,6-diynes **7a-d** [25-27], were reacted individually with propargyl alcohol (5 mol eq) in ^{t}BuOH at appropriate temperatures in the presence of the first generation pre catalysts **2a** (2 mol%), **2b** (2 mol%), and **4** (4 mol%) affording the corresponding benzene derivatives **8a-d** (Scheme 2, Table 1). Excess of propargyl alcohol was employed to effect reduction of the precatalysts to the active catalysts.



Sheme 2

Table 1. The catalytic [2+2+2]-cycloaddition of 1,6-diynes with propargyl alcohol

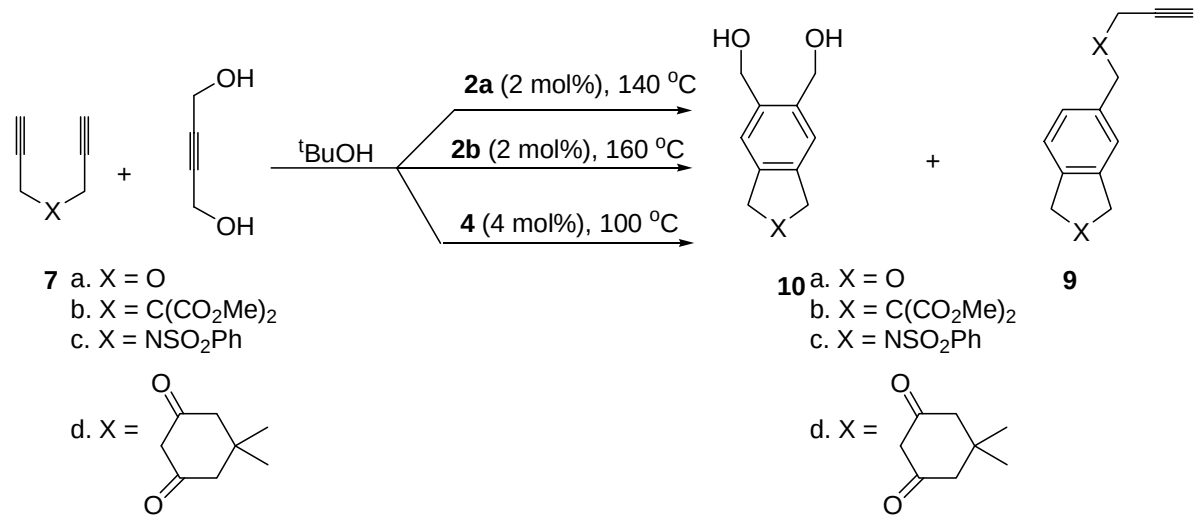
		Catalyst **2a**			Catalyst **2b**			Catalyst **4**		
Entry	Diyne	Time (h)	Conv.[a] (%)	Ratio **8**:**9**	Time (h)	Conv.[a] (%)	Ratio **8**:**9**	Time (h)	Conv.[a] (%)	Ratio **8**:**9**
1	**7a**	3	100(72)	88:12	3	100	89:11	2.5	100	82:18
2	**7b**	3	67(80)	100:0	3	68	100:0	7	100	94:6
3	**7c**	3	64(65)	81:19	18	59	85:15	3	92	89:11
4	**7d**	15	36 (83)	100:0	36	39	100:0	15	100	87:13

[a] Obtained from ^{1}H-NMR; Values given in brackets are the isolated yields of the major cycloadduct **9** (based on conversion)

Iridium precatalyst **2b** requires the highest temperature (160 °C) to promote the [2+2+2]-cycloaddition, whilst the Rh **2a** (140 °C) and Ru **4** (100 °C) precatalysts, function at lower temperatures. This temperature variation reflects the relative ease, and rate, of reduction of the precatalysts to their respective lower valent active catalysts. Another interesting feature was that

no product was observed (nmr) for 1-2 h indicating an induction period. Although the reaction showed high chemoselectivity for cycloadduct **8**, the dimer **9**, arising from the corresponding diyne, was also observed in some cases (Table 1). The diynes **7b** and **7d** afforded the corresponding cycloadducts exclusively in the presence of precatalysts **2a** and **2b**, while, 6-13% dimerisation was observed with precatalyst **4**. Diyne **7d** reacts much more slowly than diyne **7b**. Among the precatalysts evaluated for the reaction, the rate of the reaction decreased in the order Ru > Rh > Ir whilst chemoselectivity was, in general, in the reverse order.

Next we studied the [2+2+2]-cycloadditions between 1,6-diynes **7a-d** and the disubstituted alkyne, 2-butyn-1,4-diol, with the first generation precatalysts **2a, 2b** and **4** (Scheme3, Table 2).



Sheme 3

Table 2. The catalytic [2+2+2]-cycloaddition of 1,6-diynes with 2-butyn-1,4-diol

		Catalyst **2a**			Catalyst **2b**			Catalyst **4**		
Entry	Diyne	Time (h)	Conv.[a] (%)	Ratio **10**:**9**	Time (h)	Conv.[a] (%)	Ratio **10**:**9**	Time (h)	Conv.[a] (%)	Ratio **10**:**9**
1	**7a**	6	100(86)	95:5	6	100	100:0	3	100	65:35
2	**7b**	4	98 (74)	95:5	3	100	100:0	16	76	57:43
3	**7c**	4	93 (54)	71:29	27	73	100:0	8	64	44:56
4	**7d**	14	87 (65)	85:15	25	91	100:0	16	70	30:70

[a]Obtained from ^{1}H-NMR; Values given in brackets are the isolated yield of the major cycloadduct **11** (based on conversion)

Intrestingly, in the presence of precatalysts **2a** and **2b** the [2+2+2]-cycloaddition of the 1,6-diynes **7a-d** with 2-butyn-1,4-diol showed an increase in the rate of the reaction compared to those reactions with propargyl alcohol under the same reaction conditions. Furthermore precatalyst **2b** proved highly chemoselective, while precatalyst **4** showed poor chemoselectivity. This rate increase is consistent with the function of the 2-butyn-1,4-diol effecting reduction of the precatalysts to the active catalyst and in the diol case we have effectively increased the concentration of the reductant.

Next the second generation ortho-metallated Rh(III) complexes **5a,** and **6** were evaluated in the [2+2+2]-cycloaddition of **7b** with propargyl alcohol and 2-butyn-1,4-diol (Table 3). Results from the evaluation of precatalyst **2a** are also included in Table 3 for comparison.When the sterically more hindered Rh(III) complex **6** was utilised in the [2+2+2]-cycloaddition of the 1,6-diyne **7b** with propargyl alcohol and 2-butyn-1,4-diol, a decrease in the reaction temperature required to effect 100% conversion and an increase in the rate of the reaction were observed compared to the reactions effected by **2a** (Table 3, entries 4 and 7). Note that since **6** is a monomeric complex 4% of this precatalyst was added. A possible explanation for the increased activity of the precatalyst **6** could be more facile conversion of the precatalyst **6** to the active Rh(I) species (discussed in the following mechanism section). Rh(III) complex **5a** was found to be the best precatalyst among the cyclometallated complexes studied for the [2+2+2]-cycloaddition of 1,6-diynes with propargyl alcohol and 2-butyn-1,4-diol (Table 3, entries 2 and 6). No diyne dimerisation product was observed in these processes except for entry 5.

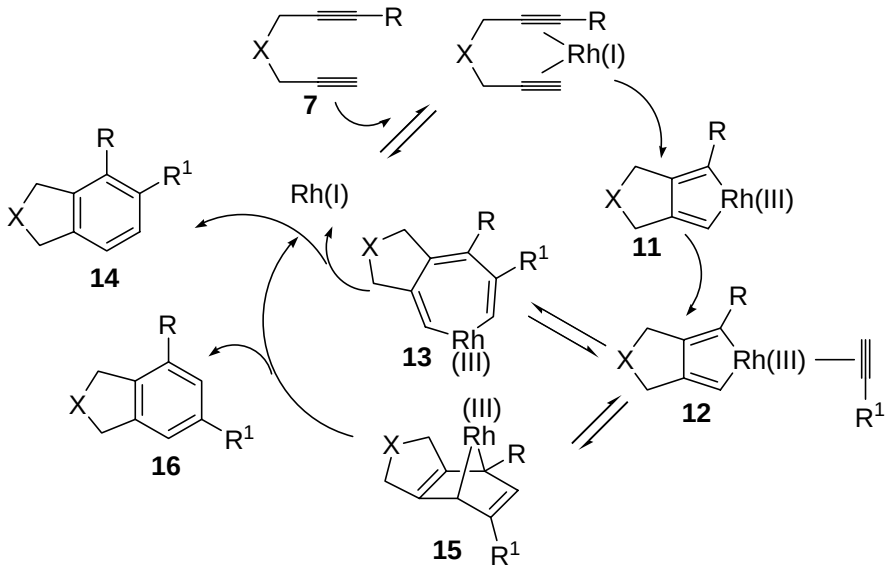
Table 3. Comparison of Rh(III) complexes for the [2+2+2-cycloaddition of 1,6-diyne **7b** with propargyl alcohol / 2-butyn-1,4-diol

Entry	Catalyst[a]	Alkyne	Time (h)	Temp. (^oC)	Conversion (%)[c]
1	**2a**	Propargyl alcohol	3	140	67
2	**5a**	Propargyl alcohol	0.5	110	100
3	**6**[b]	Propargyl alcohol	1	110	95
4	**2a**	2-butyn-1,4-diol	4	140	98[d]
5	**5a**	2-butyn-1,4-diol	0.25	110	100
6	**6**[b]	2-butyn-1,4-diol	1	110	100

[a]2 mol% catalyst was used. [b]4 mol% catalyst was used. [c]obtained from ^{1}H-NMR and no dimersation was observed. [d]5% dimer was obtained.

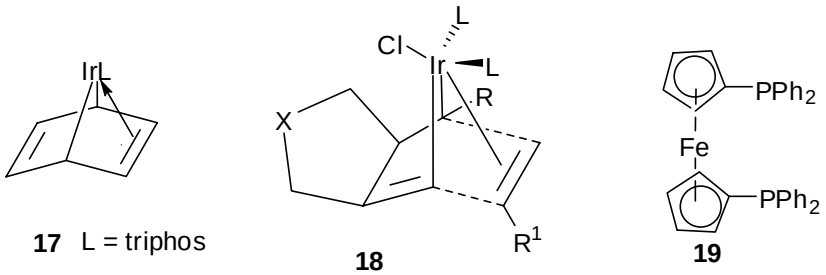
Mechanism

In our original work with Wilkinson's catalyst, which employed a series of 1,6-diynes **8** with various tethers X, we interpreted our results in terms of Scheme 4.[25]



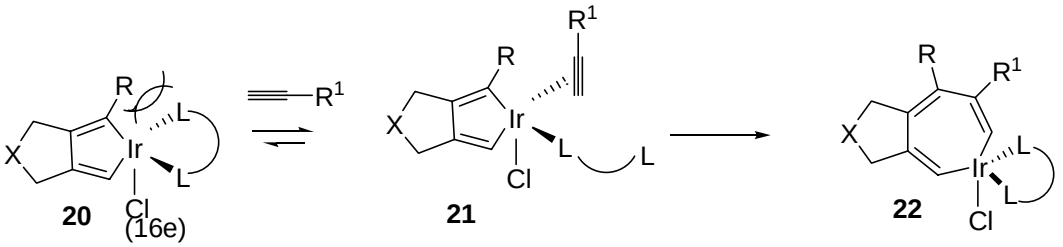
Sheme 4

Initial coordination of the rhodium(I) catalyst to the 1,6-diyne is followed by oxidative addition-cyclisation to produce the rhodacyclopentadiene complex **11**. Coordination of the monoyne then gives complex **12** which undergoes either monoyne insertion to give **13** or a Diels-Alder type reaction to give **15**. Finally, reductive elimination **13** → **14** / **15** → **16** gives the products and regenerates the Rh(I) catalytic species. In recent years the number of characterised metallocyclopentadienes[28,29] and metallocycloheptatrienes[30] has continued to expand. The unresolved problem of whether the Diels-Alder like pathway **13** → **16** (Scheme 5) or the insertion pathway **12** → **13**, or both, play a role in the [2+2+2]-cyclotrimerisation has seen some clarification. Thus crystal structures of M $(\eta^4\text{-}C_6H_6)^+$ complexes such as the fluxional triphos Ir(III) complex **17**[28c] are informative with respect to the Diels-Alder pathway.



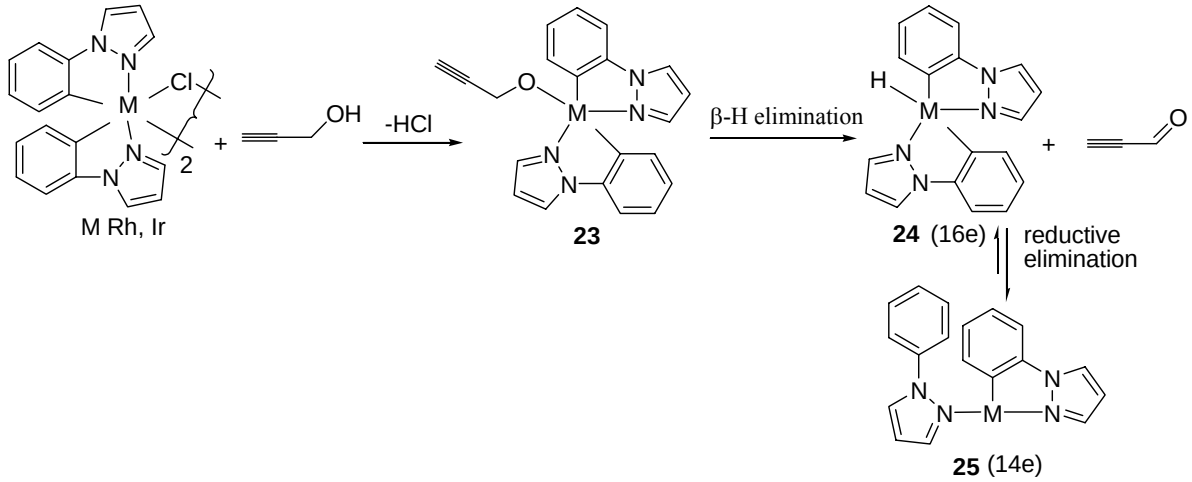
Very recently Takeuchi *et al.*[31] have provided data and mechanistic arguments that both pathways may be involved, at least when R_3P ligands are present, depending on steric effects and ligand dissociation rates. Their interpretation of factors favouring the Diels-Alder like sequence involves the incoming alkyne accessing a vacant apical Ir coordination site **18** with its

regiochemical approach trajectory minimising steric interaction between the R and R^1 groups in the reacting partners leading to the *meta*-substituted product **16** (Scheme 4). Accessing the metallocycloheptatriene pathway is believed to arise from steric hindrance in the pentacoordinate complex **20** and / or to hemilability of L favouring the equilibration **20** $\rightleftharpoons$ **21** in which steric interaction between R / R^1 is minimised. The regiochemistry of the insertion step **21** → **22** (Scheme 5) which leads to the ortho-substituted product **14**, would then suggest that Ir-C bond formation is in advance of C-C bond formation and that steric effects at Ir are the key determinant. The ferrocenyl phosphine DPPF **19** was found to be the best, of those ligands surveyed, for ortho-selectivity



Sheme 5

The cyclometallated complexes utilised in our studies differ from those normally employed in that they are M(III) (M = Ir, Rh) complexes and lack phosphine ligands. The former require an initial reductive step, to generate the catalytically active M(I) species from the respective M(III) complexes. The Ru(II) complex **4** is assumed to undergo facile reduction to ruthenium(0) nanoparticles[32] and this accounts for the lower temperature and shorter reaction times in this case. An induction period 1-2 h was observed in the [2+2+2]-cycloaddition reactions when the first generation catalysts were used which points to a slow generation of the active catalysts. A plausible pathway for the generation of M(I) species, is shown in Scheme 6. A possible explanation for the increased activity of the second generation Rh precatalysts could be the rate of conversation of the Rh(III) complex to the active Rh(I) species. In the case of precatalyst **6** this conversion may be acclerated by relief of steric strain, occasioned by the bulkiness of the ligand. Thus the active catalysts **25** in our case differ substantially from those employed previously. They should be accessible by addition of appropriate alcohol primers and their regioselectivity remains to be explored.



Sheme 6

In conclusion, we report the synthesis of a variety of novel cyclometallated Ir(III), Rh(III) and Ru(II) complexes and their catalytic activity in the [2+2+2]-cycloaddition reaction between 1,6-diynes and alkynes. The Ir(III) precatalysts complex **2b** proved highly chemoselective.

Acknowledgements

We thank Leeds University and Johnson Matthey for support.

Experimental Section

General Procedures. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Mass spectral data were obtained from a VG Autospec instrument operating at 70 eV (EI and FAB). The molecular ion peak (M^+) refers to the Ru^{102}, Ir^{193} or Cl^{35} isotope as appropriate. Accurate molecular masses were obtained from the EPSRC Swansea Mass Spectroscopy service using perfluorokerosene as an internal standard. Microanalyses were obtained using a Carbo Erba MOD11016 instrument. IR spectra were determined on a Nicolet Magna FT-IR 560 spectrometer. Nuclear magnetic resonance spectra were recorded on QE 300 and Bruker 400 instruments operating at, 300 and 400 MHz respectively and refer to solutions in $CDCl_3$ unless otherwise stated. Solvents were dried according to established methods, unless purchased dry from Aldrich in sure-seal bottles. The term ether refers to diethyl ether and the term petrol refers to the 40-60 ^oC boiling point fraction of petroleum ether. Flash column chromatography was performed over silica, Kieselgel 60 (230-400 mesh), unless otherwised

stated. Compounds **8a-d** and **2a,b** have been previously reported.[20,25-27] X-Ray data for **4** (CCDC 624678 and **6** (CCDC 628187) has been deposited in the Cambridge Crystallography Database.

Cyclometallated Hg(II) *N*-phenylpyrazole complex (3)

Utilising standard Schlenk techniques, under a dry nitrogen atmosphere, *tert*-butyllithium (4.85 ml, 8.2 mmol, 1.7 M solution in pentane) was added slowly via a syringe to *N*-phenylpyrazole (0.99 m1, 7.5 mmol) in dry petrol (15 m1), at room temperature. The mixture was stirred at room temperature for a further 12 h. The yellow precipitate was collected by filtration under a dry nitrogen atmosphere, washed with dry petrol to remove tert-butyllithium and dissolved in dry tetrahydrofuran (15 m1). Powdered mercury(II) chloride (1 .79g, 6.6 mmol) was slowly added with stirring, over the course of 30 min at -77 °C. After the addition was complete, the mixture was gradually warmed to room temperature and stirred for an additional 10 h. The resulting suspension was then filtered through celite to remove lithium chloride. The filtrate was evaporated to afford the product (1.27g, 51 %), as pale yellow solid, which was washed with petrol and used in the next step without further purification.

δ_H (DMSO-D_6): 7.91-7.66 (m, 3H, ArH), 7.55-7.31 (m, 3H, ArH) and 6.57 (m, 1H, ArH). m/z (%): 380 (M^+ [Hg^{202}], 39), 237 (8), 143 (5 1) and 77 (100).

Cyclometallated Ru(II) *N*-phenylpyrazole complex (4)

a. A suspension of di-μ-chlorobis[(p-cymene)chlororuthenium(II)] (0.93g, 1.5 mmol) and the cyclometallated mercury(II) complex 3 (1.15g, 3 mmol) in anhydrous acetonitrile (l00 ml) was stirred at ambient temperature under a blanket of dry nitrogen for 24 h. The solution was filtered and the filtrate evaporated on a rotary evaporator. The residue was dissolved in a minimum amount of dichloromethane and subjected to flash column chromatography over a short column of alumina, which had been packed with ether. Elution with chloroform and evaporation of the solvent under reduced pressure afford the product (0.76g, 61 %) as shiny, brown plates, m.p. 181-184 °C (dec.). δ_H: 8.13 (dd, 1H, J 7.3 and 1.2 Hz, ArH), 8.05 and 7.91 (2 x d, 2 x 1H, J 2.4 Hz, ArH), 7.18-7.00 (m, 3H, ArH), 6.47 (t, 1H, J 2.4 Hz, ArH), 5.55 (d, 2H, J 6.1 Hz, ArH), 5.28 and 5.08 (2 x d, 2 x 1H, J 6.1 Hz, ArH), 2.43 (m, 1H, $CHMe_2$), 2.0 4 (s, 3H, Me), 0.96 and 0.92(2 x d, 2 x 3H, J 6.9 Hz, $CHMe_2$). m/z (%): 414 (M^+, 18), 379 (7), 280 (24), 143 (6), 134 (26) and 119 (100). ν_{max}/cm^{-1} (nujol): 848 and 744. HMRS Found: 379.0741 ($C_{19}H_{21}N_2Ru$ – Cl) requires: 379.0743

b. [Ru(p-cymene)Cl_2]$_2$ (0.1042g, 0.17mmol), N-phenylpyrazole (0.0482g, 0.33mmol) and sodium acetate (0.0341g, 0.42mmol) in DCM (20 ml) were stirred at room temperature for 24 hThe mixture was then evaporated, leaving a brown residue, which was crystallised from DCM and hexane to afford **4** as pale brown needles in (0.099g 73%).

General procedure for cyclometallated complexes of rhodium(III) and iridium(III)

Either rhodium(III) chloride hydrate or iridium(III) chloride hydrate (2.5 mmol) was added to the appropriate ligand (6 mmol) in 2-methoxyethanol (25 m1*)* and the mixture boiled under reflux

for the appropriate time. The resulting suspension was filtered to afford the product, which was further purified by crystallisation if necessary.

Cyclometallated Rh(III) 2-phenylbenzothiazole complex (5a). Rhodium(III) chloride hydrate (0.52g, 2.5 mmol) and 2-phenylbenzothiazole (1.27g, 6 mmol) were mixed in 2-methoxyethanol (25 m1) and heated at 125 ^{o}C) under reflux for 16 h. The precipitated product was filtered and washed with ether followed by n-hexane to afford the product (1 .08g, 77 %) as a yellow powder, m.p. >230 ^{o}C.

Found: C, 55.70; H,2.75; Cl, 6.4 50; N,5.15; $C_{52}H_{32}C1_2N_4Rh_2S_4$ requires: C, 55.87; H, 2.89; Cl, 6.34; N, 5.01%. δ_H (DMSO-D_6): 9.4 (br, 2H), 8.21(d, 2H, J 7.4 Hz, ArH), 7.66-7.47 (m, 6H, ArH), 6.85 and 6.68 (2 x t, 2 x 2H, J 7.4 Hz, ArH) and 6.08 (d, 2H, J 7.4 Hz, ArH). m/z (%) (FAB): 558 (M^+ monomer], 1), 523 (1), 348 (1), 210 (1) and 157 (100).

Cyclometallated Ir(III) complex 2-phenylbenzothiazole (5b). Iridium(III) chloride hydrate (0.75g, 2.5 mmol) and 2-phenylbenzothiazole (1.27g, 6 mmol) were mixed in 2-methoxyethanol (25ml) and heated at 125 ^{o}C under reflux for 16 h. The precipitated product was filtered and washed with ether to afford the product (1 .3g, 86 %), as an orange powder, m.p. >230 ºC.

Found: C, 47.30; H, 2.55; Cl, 5.80; N, 4.25; $C_{52}H_{32}Cl_2Ir_2N_4S_4.1M\ H_2O$ requires: C,47.51; H, 2.61;Cl, 5.40; N, 4.26 %. δ_H (DMSO-D_6): 8.24 (d, 4H, J 7.5 Hz, ArH), 8.1 1-8.00 (m, 4H, ArH), 7.70-7.50 (m, 16H, ArH), 6.83 and 6.62 (2 x brs, 2 x 4H, ArH). m/z (%), (FAB): 648(M^+ monomer, 1), 613 (3), 438 (1), 232 (100) and 210 (1). ν_{max}/cm^{-1} (nujol): 1579, 752 and 739.

Cyclometallated Rh(III) 3,5-dimethyl-2-phenylpyrazole complex (6). Rhodium(III) chloride hydrate (1.05g, 5 mmol) and 3,5-dimethyl-2-phenylpyrazole (2.06g, l2 mmol) were mixed in 2-methoxyethanol (50 m1) and heated at 125 ^{o}C under reflux for 24 h. On cooling to room temperature, the product, (1 .25g, 45 %), crystallised from the reaction mixture as colourless needles, m.p. >230 ºC.

Found: C, 53.75; H, 5.40; N, 9.95; Cl, 6.30; $C_{22}H_{22}C1N_4Rh.C_3H_8O_2$ requires: C, 53.90; H, 5.45; N, 10.05; Cl, 6.35%. δ_H 7.22 (d, 2H, J 7.3 Hz, ArH), 6.83 and 6.60 (2 x t, 2 x 2H, J 7.3Hz, ArH), 6.20 (d, 2H, J 7.3 Hz, ArH), 6.07 (s, 2H, ArH), 3.75-3.70 (m, 2H, OCH_2), 3.50 (t, 2H, J 4.5Hz, OCH_2), 3.39 (s, 3H, OMe), 2.72 (s, 6H, 2xMe), 2.32 (brs, 6H, 2xMe) and 1.96 (t, 1H, J 6.1Hz, OH). m/z (%), (FAB): 480 (M^+-$C_3H_8O_2$, 13), 445 (100), 309 (4) and 17 1(1). ν_{max}/cm^{-1} (nujol): 3286, 1111. 1045 and 748.

General procedure for cyclisation of 1,6-diynes with monoynes

1,6-Diyne, monoyne and the catalyst were mixed in tert-butanol in a Schlenk tube and stirred and heated at the appropriate temperature for the appropriate time. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography to afford the product.

(1,3-Dihydro-2-benzofuran-5-yl)methanol (8a)

2,2-Diprop-2$^{'}$-ynylether (0.024g, 0.25 mmol), propargyl alcohol (73 µl, 1.25 mmol) and 2a

(4.6 mg, 0.005 mmol) were mixed in tert-butanol (7 m1) and stirred at 140 °C for 3 h. After removing the solvent the residue was purified by flash column chromatography, eluting with 1:4 v/v ether-petrol to afford the product (0.027g, 72 % based on 100 % conversion) as a white powder, m.p. 68-70° C (Lit.[25] 70-71 °C).

δ_H: 7.24-7.21 (m, 3H, ArH), 5.1 1 (s, 4H, 2 x CH_2) and 4.71 (s, 2H, CH_2OH). m/z (%): 150 (M^+, 67), 133 (5), 119 (32) and 91 (100).[25]

Catalyst (2b). (5.1mg, 0.005 mmol) heating at 160 °C for 3 h gave the product 89 %

Catalyst (4). (4.1mg, 0.01 mmol) heating at 100 °C for 2.5 h gave the product 82 %

Dimethyl 5-hydroxymethyl-1,3-dihydro-2*H*-indene-2,2-dicarboxylate (8b)

A mixture of dimethyl 2,2-diprop-2'-ynylmalonate (0.05g, 0.25 mmol), propargyl alcohol (73 µl, 1.25 mmol) and 2a (4.6mg, 0.005 mmol) in tert-butanol (7 m1) was stirred and heated at 140 °C for 3 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with 1:1 v/v ether-petrol to afford the product (0.07g. 80 % based on 67 % conversion) as a colourless, thick oil.

Found: C, 63.35; H, 6.20; $C_{14}H_{16}O_5$ requires: C, 63.65; H, 6.10 %. δ_H 7.20-7.l5 (m, 3H, ArH), 4.61 (s, 2H, CH_2OH), 3.73 (s, 6H, 2 x CO_2Me) and 3.57 (s, 4H, 2 x CH_2). m/z (%): 264 (M^+, 37), 233 (7), 205 (50), 204 (100) and 59 (46). ν_{max}/cm^{-1} (nujol): 3514, 1753, 1724, 1281, 1077 and 1046.

Catalyst (2b). (5.1 mg, 0.005 mmol) heating at 160 °C for 3 h gave 68 % of product based on 68 % conversion.

Catalyst (4). (4.1 mg, 0.001 mmol) heating at 100 °C for 7 h gave the product 94 %

Catalyst (5a). (5.6 mg, 0.005 mmol) heating at 110 °C for 30 min gave the product in quantitative yield.

Catalyst (6). (9.6 mg, 0.01 mmol) heating at 110 ºC for l h gave 95 % of product based on 95 % conversion.

(*N*-Phenylsulfonyl-2,3-dihydro-1*H*-isoindol-5-yl)methanol (8c)

N,*N*-Diprop-2-ynylphenylsulphonamide (0.058g, 0.25 mmol), propargyl alcohol (73µl, 1.25 mmol) and catalyst 2a (4.6 mg, 0.005 mmol) were mixed in tert-butanol (7 ml) and stirred at 140 °C for 3 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with 3:1 v/v ether-ethyl acetate, followed by crystallisation from ether and dichloromethane (trace) to afford the product (0.03g, 66 % based on 64 % conversion) as a white powder, m.p. 97-99 °C.

Found: C, 58.70; H, 5.20; N, 5.00; $C_{15}H_{15}NO_3S$ requires: C, 62.26; H, 5.23; N, 4.84 %. δ_H 7.88-7.84 (m, 2H, ArH), 7.57-7.47 and 7.25-7.11(2 x m, 2 x3 H, ArH), 4.64 (s, 2H, CH_2OH) and 4.59 (s, 4H, 2 x CH_2). m/z (%): 289 (M^+, 21), 148 (100), 141 (21), 77 (88) and 51 (37).

Catalyst (2b). (5.1 mg, 0.005 mmol) heating at 160 °C for 18 h gave the product 50 % based on 59 % conversion.

Catalyst (4). (4.1 mg, 0.01 mmol) heating at 100 °C for 3h gave the product 82 % based on 92 % conversion.

(*N*-Benzenesulfonyl-2,3-dihydro-1H-isoindol-5yl)-methanol (8d)

2,2-Diprop-2'-ynyldimedone (0.054g, 0.25 mmol), propargyl alcohol (73µl, 1.25 mmol) and catalyst 2a (4.6mg, 0.005 mmol) were mixed in tert-butanol (7 m1) and stirred at 140 °C for 15 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with ether to afford the product (0.02g, 83 % based on 36 % conversion) as a white powder, m.p. 157-159 °C (Lit.[25] 158-159 °C).

δ_H 7.18-7.14 (s, 3H, ArH), 4.63 (d, 2H, J 5.3 Hz, CH_2OH), 3.44 (s, 4H, 2 x CH_2), 2.70 (s, 4H, 2 x CH_2CO) and 1.04 (s, 6H, 2 x Me). m/z (%): 272 (M^+, 7), 255 (4), 188 (34) and 115 (38).

Catalyst (2b). (5.1 mg, 0.005 mmol) heating at 160 °C for 36 h gave the product 39 % based on 39 % conversion.

Catalyst (4). (4.1 mg, 0.01 mmol) heating at 100 °C for 15 h gave the product 89 %.

(6-Hydroxymethyl-1,3-dihydro-2-benzofuran-5-yl)methanol (10a)

Diprop-2-ynylether (0.024g, 0.25 mmol), 2-butyn-1,4-diol (0.065g, 0.75 mmol) and the catalyst 2a (4.6 mg, 0.005 mmol) were mixed in tert-butanol (7 m1) and stirred at 140 °C for 6 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with ether to afford the product (0.039g, 86 %) as a pale yellow, thick gum.

Found: C, 66.35; H, 6.50; $C_{10}H_{12}O_3$ requires: C, 66.65; H, 6.71 %.δ_H: 7.21 (s, 2H, ArH), 5.05 (s, 4H, 2 x CH_2), 4.71 (s, 4H, 2 x CH_2OH) and 3.37 (brs, 2H, 2 x OH). m/z (%): 180(M^+,1), 163 (12), 149 (16) and 57 (100). ν_{max}/cm^{-1} (nujol): 3272, 1181 and 1073.

Catalyst (2b). (5.1mg, 0.005 mmol) heating at 160 °C for 6 h gave the product in quantitative yield

Catalyst (4). (4.1 mg, 0.01 mmol) heating at 100 °C for 3 h gave the product 65 %.

Dimethyl 5,6-bis(hydroxymethyl)-1,3-dihydro-2H-indene-2,2-dicarboxylate (10b)

Dimethyl 2,2-diprop-2'-ynylmalonate (0.05g, 0.25 mmol), 2-butyn- 1 ,4-diol (0.065g, 0.75 mmol) and catalyst **2a** (4.6mg, 0.005 mmol) were mixed in tert-butanol (7 ml) and stirred at 140 °C for 4 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with ether to afford the product (0.053g, 74 % based on 98 % conversion) as a pale yellow gum.

Found: C,60.95; H, 6.50; $C_{15}H_{18}O_6$ requires: C, 61.22; H, 6.16 %. δ_H: 7. 14 (s, 2H, ArH), 4.59 (d, 4H, J 4.3 Hz, 2 x CH_2OH), 3.72 (s, 6H, 2 x CO_2Me) and 3.55 (s, 4H, 2 x CH_2). m/z (%): 294 (M^+, 14), 277 (20), 263 (9), 235 (38), 216 (100) and 59 (53).

Catalyst (2b). (5.1mg, 0.005 mmol) heating at 160 °C for 3 h gave the product in quantitative yield.

Catalyst (4) (4.1 mg, 0.01 mmoI) heating at 100 °C for 16 h gave the product 43 % based on 76 % conversion.

Catalyst (5a). (5.6mg, 0.005 mmol) heating at 110 °C for 15 min gave the product in quantitative yield

Catalyst (6). (9.6mg, 0.01 mmoI) heating at 110 °C for l h gave the product in quantitative yield.

(*N*-Benzenesulfonyl-6-hydroxymethyl-2,3-dihydro-1H-isoindol-5-yl)methanol (10c)

N,*N*-Diprop-2-ynylphenylsulphonamide (0.058g, 0.25 mmol), 2-butyn-1,4-diol (0.065g, 0.75 mmol) and catalyst 2a (4.6mg, 0.005 mmol) were mixed in tert-butanol (7 ml) and stirred at 140 °C for 4 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with 1:1 v/v ether-ethyl acetate, followed by crystallisation from dichloromethane to afford the product (0.04g, 54 % based on 93 % conversion) as a pale yellow powder, m.p. 109-112 °C.

Found: C,59.90; H, 5.45; N, 4.20 $C_{16}H_{17}NO_4S$ requires: C, 60.17; H, 5.37; N, 4.39 %. δ_H 7.89-7.85 (m, 2H, ArH), 7.58-7.48 (m, 3H, ArH), 7.17 (s, 2H, ArH), 4.68 (s, 4H, 2 x CH_2OH), 4.59 (s, 4H, 2 x CH_2) and 4.28 (s, 2H, 2 x OH). m/z (%): 319 (M^+, 15), 302 (9), 288 (5), 141 (27), 77 (100) and 51 (46). ν_{max}/cm^{-1} (nujol): 3299, 1343, 1162, 758 and 689.

Catalyst (2b). (5.1 mg, 0.005 mmol) heating at 160 °C for 27 h gave the product 73 % based on 73 % conversion.

Catalyst (4). (4.1 mg, 0.01 mmol) heating at 100 °C for 8 h gave the product 28 % based on 64 % conversion.

5',6'-Bis(hydroxymethyl)-4,4-dimethyl-1'3'-dihydro-2H,^H-spiro[cyclohexane-1,2'-indene]-2,6-dione (10d)

2,2-Diprop-2'-ynyldimedone (0.054g, 0.25 mmol), 2-butyn-1,4-diol (0.065g, 0.75 mmol) and catalyst 2a (4.6 mg, 0.005 mmol) were mixed in tert-butanol (7 m1) and stirred at 140 °C for 14 h. After removing the solvent, the residue was purified by flash column chromatography, eluting with 4:l v/v ether-ethyl acetate to afford the product (0.042 g, 65 % based on 87 % conversion) as a white powder, m.p. 142-145 °C.

Found: C, 71.25; H, 7.55; $C_{18}H_{22}O_4$ requires: C, 71.50; H, 7.33 %. δ_H 7.15 (s, 2H, ArH), 4.66 (s, 4H, 2 x CH_2OH), 3.43 (s, 4H, 2 x CH_2), 2.91 (brs, 2H, 2 x OH), 2.70 (s, 4H, 2 x CH_2CO) and 1.04 (s, 6H, 2 x Me). m/z(%): 302(M^+, 14), 285 (5), 2 18 (100), 128 (46) and 115 (38). ν_{max}/cm^{-1} (nujol): 3468, 1724 and 1071.

Catalyst (2b). (5.1 mg, 0.005 mmol) heating at 160 °C for 25 h gave the product 91 % based on 91 % conversion.

Catalyst (4). (4.1 mg, 0.01 mmol) heating at 100 °C for 16 h gave the product 21 % based on 70 % conversion.

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