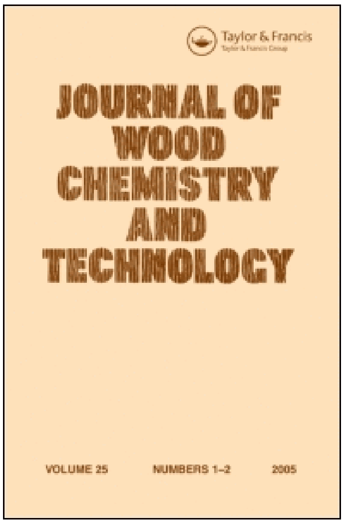

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REACTIONS OF METAL ION COMPLEXES WITH LIGNIN MODEL COMPOUNDS, PART III. Rh(TSPP) CATALYZED FORMATION OF GUAIACOL FROM β-ARYL ETHERS IN EXCEPTIONALLY HIGH YIELD.

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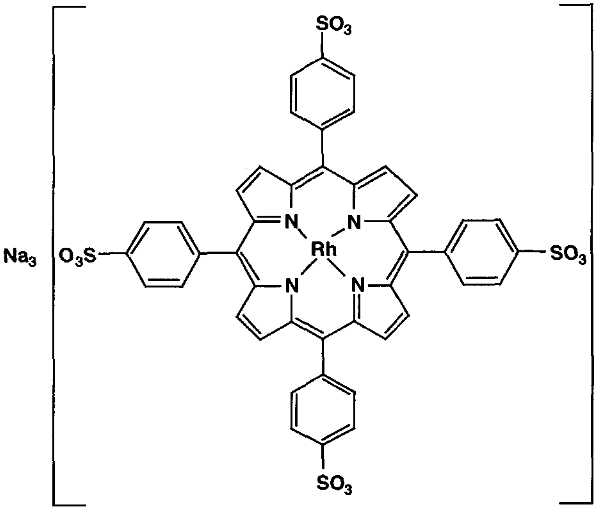
ABSTRACT

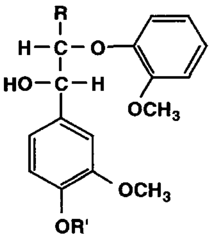
Trisodium meso-tetra-4-sulfonatophenylporphinerhodium(III) (Rh(TSPP)) was found to be a very effective catalyst for cleaving the β-aryl ether bonds of the lignin model compounds guaiacylglycol β-guaiacyl ether (**1**) and guaiacylglycerol β-guaiacyl ether (**11**). In both cases very large amounts of guaiacol (**2**) were formed regardless of whether the reducing sugar glucose was present or not. With the substituted phenylethane model **1** the other major product was acetovanillone (**5**); with the substituted phenylpropane model **11** considerable amounts of vanillin (**4**) were formed. The products obtained with the rhodium catalyst were very different to those formed in the Co(TSPP) or anthraquinone (AQ) catalyzed reactions. They were, however, similar to those obtained with Fe(TSPc), although the rhodium catalyst was much more active and formed guaiacol at a much faster rate. In addition to these reactions, the rhodium complex also catalyzes the partial demethylation of the 3,4-dimethoxyphenyl model compound **10**. Mechanisms are proposed for these reactions in which the key steps involve single electron transfer between the catalyst and the substrate.

INTRODUCTION

Investigations of a number of first row transition metal porphyrin and phthalocyanine complexes have revealed that Co(TSPP) and Fe(TSPc) are both very effective catalysts for the cleavage of β-aryl ether bonds in the lignin model compounds **1** and **11**.[1-3] The iron catalyst is also capable of forming oxidized products in the absence of added oxidant. In an extension of this work we now



Trisodium meso-tetra-4-sulfonatophenylporphinerhodium(III) (Rh(TSPP))



R=H, R'=H;	guaiacylglycol β-guaiacyl ether (1)
R=H, R'=CH_3;	veratrylglycol β-guaiacyl ether (10)
R=CH_2OH, R'=H;	guaiacylglycerol β-guaiacyl ether (11)

FIGURE 1. The catalyst Rh(TSPP) and lignin model compounds **1**, **10** and **11**

report the results of our studies of the second row metalloporphyrins Rh(TSPP) and Ru(CO)(TSPP).

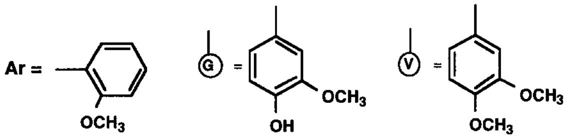
RESULTS AND DISCUSSION

Reactions Of The Phenolic β-Ether Lignin Model Compound **1**

Reactions of the lignin model compounds **1** and **11** were carried out under the same conditions as those previously used with the catalysts Co(TSPP) and Fe(TSPc) (see the two preceding papers Parts I and II of this series).[4,5] The total product analysis for each of the reactions with **1** is given in Table 1. The results obtained for the AQ catalyzed reactions are also included for comparison. The

TABLE 1. Total Reaction Component Analysis for **1**[a]

	H | Ⓖ	CH_2 ‖ CH | Ⓖ	CHO | Ⓖ	CH_3 | C=O | Ⓖ	CH_3 | CHOH | Ⓖ	CHOAr ‖ CH | Ⓖ	CH_2OAr | C=O | Ⓖ	CH_2OAr | CHOH | Ⓖ
Catalyst	%**2**	%**3**	%**4**	%**5**	%**6**	%**7**	%**8**	%**1**
Control	23		3			37		40
Control/Gl	33	4			1	29		32
AQ	30	9	4	1	2	16		10
AQ/Gl	65	18	1	2	5	2		17
Ru(CO)(TSPP)/Gl	37	7		2	2	18	1	10
Rh(TSPP)	88			74				
Rh(TSPP)/Gl	86	7	1	46	3			



Gl = glucose, **AQ** = anthraquinone

[a] Conditions: 135°C, N_2, 1 M NaOH, 2hr; control = 1 M NaOH solution alone. mole ratios, model compound : catalyst : glucose = 1 : 0.1 : 2.15

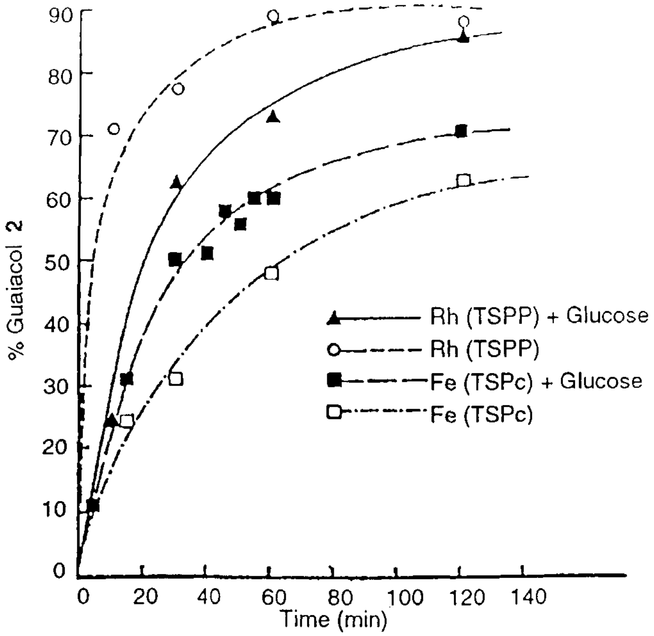


FIGURE 2. Guaiacol (**2**) Formation as a Function of Time for the Rh(TSPP) and Fe(TSPc) catalyzed Reactions of **1**

complex Ru(CO)(TSPP) displayed little catalytic activity in the presence of added glucose and so its reactions were not investigated further. In contrast, Rh(TSPP) was extremely active and produced very high yields of guaiacol (**2**) both with and without added glucose. The other remarkable feature of these reactions, aside from the large amounts of acetovanillone (**5**) formed, was that only very minor quantities of other products were detected.

In view of the high activity of the rhodium catalyst, the rates of formation of guaiacol (**2**) and acetovanillone (**5**) were investigated. The results are presented in Figures 2 and 3 along with the comparative values for Fe(TSPc). After only 10 minutes at 135°C in 1M NaOH solution the Rh(TSPP) catalyst formed a 71% yield of guaiacol (**2**). Under the same conditions the Fe(TSPc)

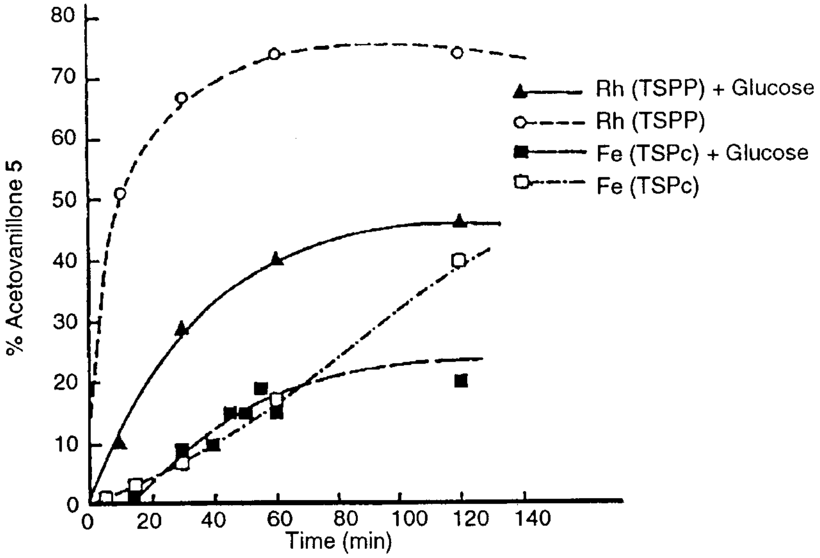
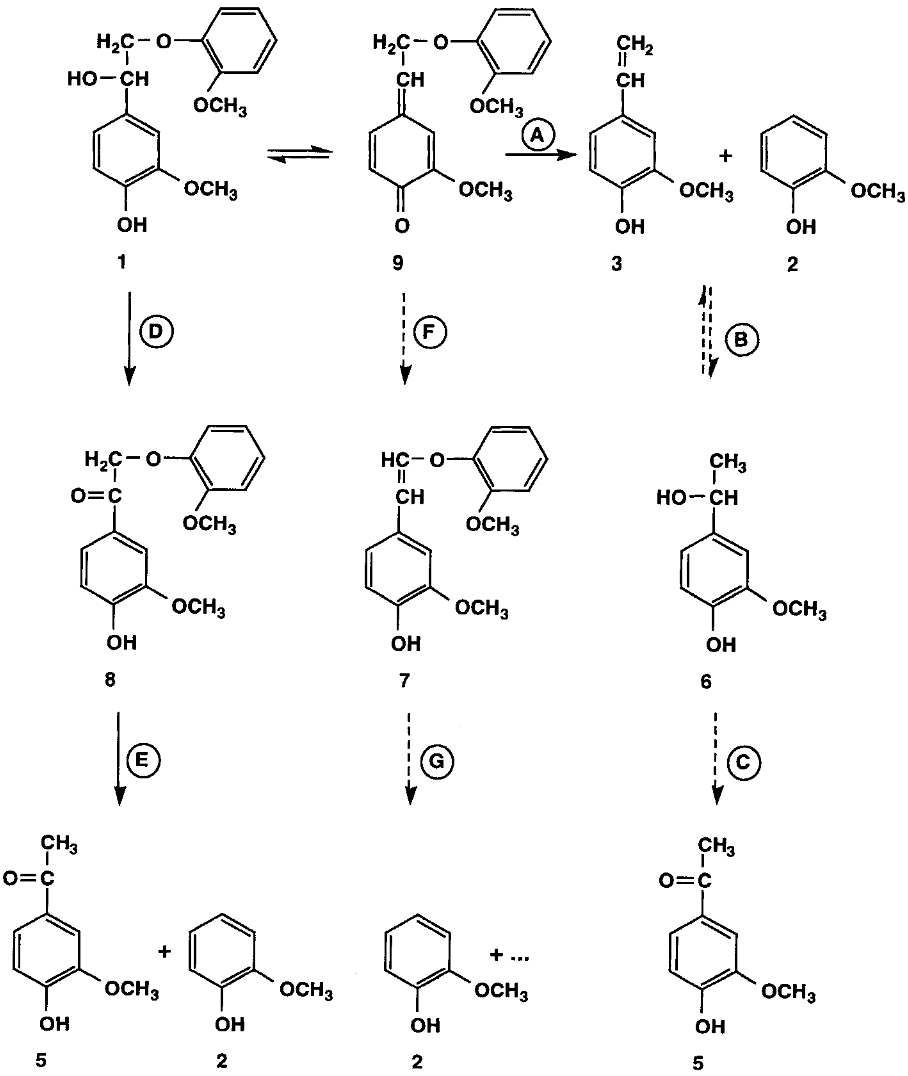


FIGURE 3. Acetovanillone (5) Formation as a Function of Time for the Rh(TSPP) and Fe(TSPc) catalyzed Reactions of **1**

catalyst produced only 18% guaiacol (**2**). Surprisingly, in the presence of added glucose guaiacol (**2**) formation was not as rapid for Rh(TSPP) with only 24% being released after 10 minutes. Acetovanillone (**5**) was formed at comparable rates to guaiacol (**2**) in both reactions.

The formation of these products can be rationalized in terms of the general pathways depicted in Scheme 1. The products of the reactions of **1** with the catalysts Co(TSPP) and Fe(TSPc) have been discussed in terms of the same Scheme.[4,5]

On heating Rh^{III}(TSPP) with glucose in 1 M sodium hydroxide solution at 135°C, complete reduction to $[Rh^{II}(TSPP)]_2$ occurred.[6] The reaction was monitored by UV-vis spectroscopy. This reduced species has previously been formed in alkaline solution using pulse radiolysis. Under these conditions,



SCHEME 1. Rationalization of the Product Distribution Obtained from Reaction of **1** with Rh(TSPP)

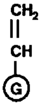
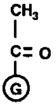
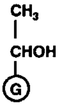
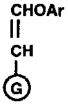
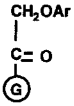
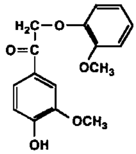
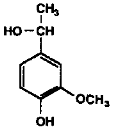
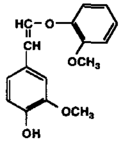
dimerization rapidly followed the initial formation of Rh^{II}(TSPP). Importantly, further reduction by one electron gave a species which had only a transient existence and was rapidly decomposed by reaction with water. No Rh^{I}(TSPP) was observed to form.[6] Thus, for the reactions of **1** at 135°C in the presence of glucose, $[Rh^{II}(TSPP)]_2$ (or the monomer Rh^{II}(TSPP)) is most likely the dominant, catalytically active species. The relatively small amount of guaiacol (**2**) formed in the reactions of the non-phenolic lignin model compound **10** (Table 3) suggests that reaction of the quinone methide **9** with $[Rh^{II}(TSPP)]_2$ (pathway A, Scheme 1) is one route to guaiacol (**2**) formation in the reactions of **1**. The other product formed in this pathway is vinyl guaiacol (**3**) and a small amount (7%) was detected in the total product distribution from **1** (Table 1). Vinyl guaiacol (**3**) is reactive under the conditions used and so the amount isolated at the end of the reaction would not have reflected the total that was formed. The mechanism of the reaction between the quinone methide **9** and the reduced catalyst is probably the same as that proposed for Co^{II}(TSPP),[4] with the key step involving single electron transfer to the qinone methide followed by cleavage of the β-aryl ether bond.

Reactions Of Proposed Intermediate Compounds.

Reactions of the other potential intermediate compounds derived from **1** (Scheme 1) were investigated and the results are given in Table 2. Apocynol (**6**) produced some acetovanillone (**5**), especially in the absence of added glucose. Thus Rh^{III}(TSPP) is capable of oxidizing apocynol (**6**) and in this respect it is very similar to Fe^{III}(TSPc). The small amount of acetovanillone (**5**) formed in the presence of added glucose indicates that pathways B and C in Scheme 1 are not important routes to acetovanillone (**5**) in the reactions of **1** with Rh(TSPP)/ glucose as catalyst. The other product of note from apocynol (**6**) was guaiacol (**2**) (13%). The amount formed was independent of added glucose. Neither Co(TSPP) nor Fe(TSPc) produced guaiacol (**2**) from **6**.[4,5]

The vinyl ether **7** also yielded considerable quantities of guaiacol when reacted with the rhodium catalyst. In addition, minor amounts of a number of

TABLE 2. Products from Proposed Intermediate Compounds[a]

		 $H-G$	 $CH_2=CH-G$	 $CHO-G$	 $CH_3-C(=O)-G$	 $CH_3-CHOH-G$	 $CHOAr=CH-G$	 $CH_2OAr-C(=O)-G$
	Catalyst	%**2**	%**3**	%**4**	%**5**	%**6**	%**7**	%**8**
 **8**	Control	9						89
	Control/Gl	11			5			87
	Rh(TSPP)	29			21			56
	Rh(TSPP)/Gl	90			86			
 **6**	Control		29			10		
	Control/Gl		24			12		
	Rh(TSPP)	13	15	1	19	7		
	Rh(TSPP)/Gl	13	15		4	7		
 **7**	Control	9					65	
	Control/Gl	7					31	
	Rh(TSPP)	41	3	4	5	1	10	
	Rh(TSPP)/Gl	37	7	2	5	3	14	

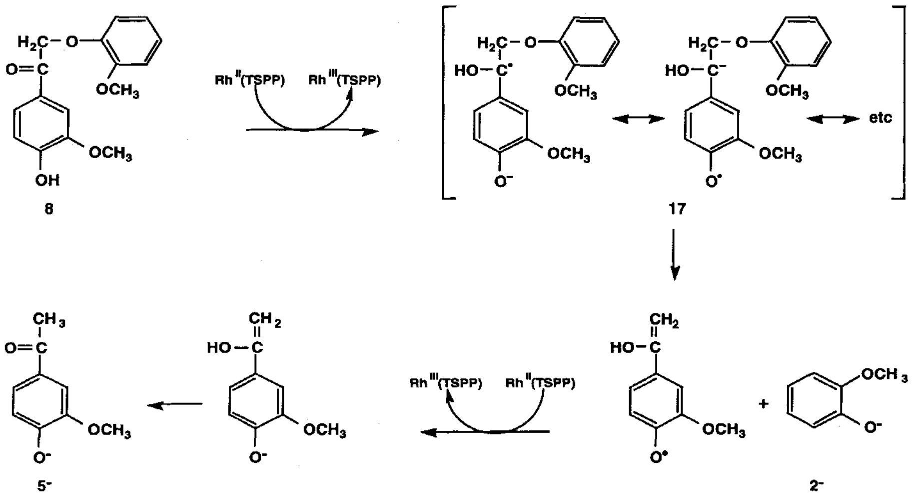
[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

other products were formed. Significantly, some of the starting compound **7** remained at the conclusion of both the reactions with and without added glucose. However, no **7** was detected in the products of **1** (Table 1). This suggests that pathway F in Scheme 1 is unimportant here.

Reactions of the α-carbonyl compound **8** with the Rh(TSPP)/glucose catalyst resulted in almost quantitative conversion to guaiacol (**2**) (90%) and acetovanillone **5** (86%) (Table 2). No unreacted **8** remained at the conclusion of the reaction and no other products were detected. In contrast, reaction of **8** with the rhodium catalyst in the absence of added glucose produced only modest amounts of these two compounds. Thus a plausible route to guaiacol (**2**) and acetovanillone (**5**) in the Rh^{III}(TSPP) catalyzed reaction of **1** in the absence of added glucose is via pathways D and E of Scheme 1. Oxidation of **1** to **8** generates the reduced catalyst $[Rh^{II}(TSPP)]_2$ which then reacts with **8** producing guaiacol (**2**) and acetovanillone (**5**). The α-carbonyl compound **8** must successfully compete with the quinone methide **9** for the reduced catalyst. Compound **8** was not detected as one of the products derived from **1**, presumably because its reaction with the reduced catalyst is so efficient. However, the fact that Rh^{III}(TSPP) can oxidize the α-hydroxyl group in apocynol (**6**) to give acetovanillone (**5**) (Table 2) indicates that pathway D in Scheme 1 is feasible. The iron catalyst, Fe^{III}(TSPc), is also efficient at oxidizing **1** to **8**, although the subsequent β-ether cleavage reaction to yield **2** and **5** is slow and thus **8** accumulates in the products.[5] In contrast, Co^{III}(TSPP) is not efficient at oxidizing **1** although Co^{II}(TSPP) does react with preformed **8** to give **2** and **5** exclusively.[4]

Pathways D and E of Scheme 1 might still operate to some extent in the Rh(TSPP)/glucose catalyzed reaction of **1**. A relatively large amount of acetovanillone (**5**) (46%) was observed to be formed in this reaction (Table 1). As pathways B and C (Scheme 1) appear to be relatively unimportant for this catalyst (see above) some of the acetovanillone (**5**) must be formed via pathways D and E. For this to happen, **1** must compete with glucose as a reductant for Rh^{III}(TSPP) and **8** must compete with the quinone methide **9** as an oxidant for the reduced cataylst.

The mechanism of the oxidation of **1** by Rh^{III}(TSPP) (pathway D) is probably the same as that already described for Fe^{III}(TSPc).[5] The proposed mechanism for pathway E is depicted in Scheme 2. The initial step involves a single electron transfer from the reduced rhodium catalyst to **8**. Subsequent cleavage of the radical intermediate **17** then gives the guaiacol anion and the enolized acetovanillone radical. Further electron transfer to this latter species, followed by tautomerization gives the acetovanillone anion. The species **17** is



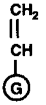
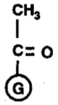
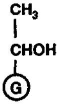
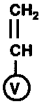
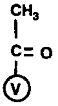
(Note: the actual reductant may be $[Rh^{II}(TSPP)]_2$, see text)

SCHEME 2. Proposed Mechanism for the Formation of **2** and **5** from **8**

very similar to the intermediate proposed in the first step of the mechanism for the reaction of the quinone methide **9** with $Co^{II}(TSPP)$.[4] Precedents for the cleavage reactions of species such as **17** have been discussed before.[7]

The reduced catalysts $Co^{II}(TSPP)$ and $Fe^{I}(TSPc)$ also react with the α–carbonyl compound **8**, giving both acetovanillone (**5**) and guaiacol (**2**) in approximately equal amounts as the only products.[4,5] However, the activity of each of these two catalysts is much less than that of the rhodium catalyst. Although the possibility exists that both $[Rh^{II}(TSPP)]_2$ and $Fe^{I}(TSPc)$ could react with **8** via a mechanism involving adduct formation followed by breakdown with transfer of two electrons from the catalyst, $Co^{II}(TSPP)$ cannot react this way. A mechanism involving single electron transfer is the only reasonable possibility for this catalyst.[4] The similarity in the product distributions for all three reduced catalysts is consistent with a common mechanism, and therefore the single electron transfer mechanism in Scheme 2 is favoured for all three catalysts.

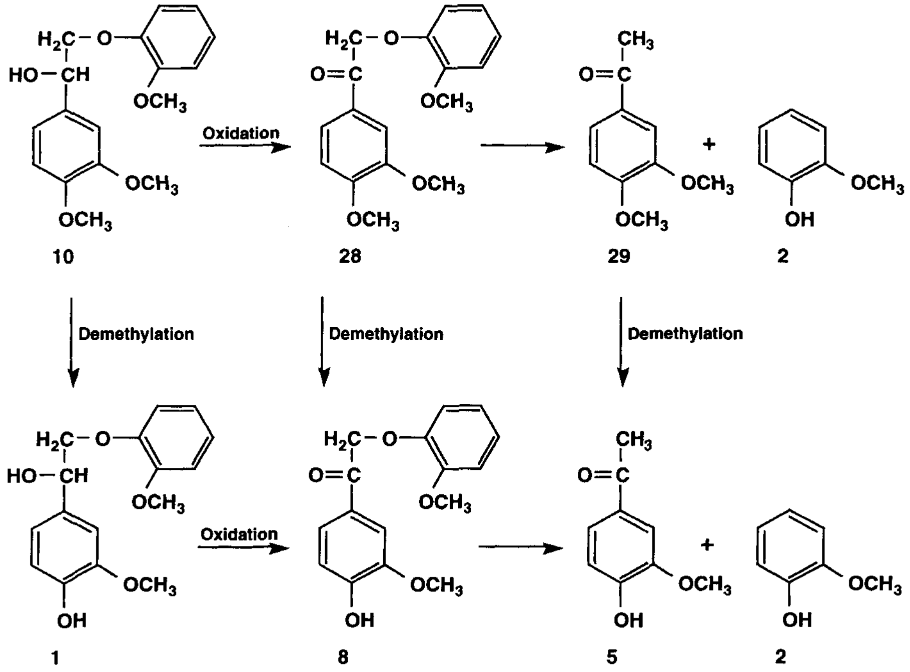
TABLE 3. Products from the Non-phenolic Model Compound **10**[a]

						
Catalyst	%**2**	%**3**	%**5**	%**6**	%**27**	%**29**
Control	3					
Control/Gl	10					
AQ/Gl	17				3	
Rh(TSPP)	28		17			6
Rh(TSPP)/Gl	28	4	9	2		4

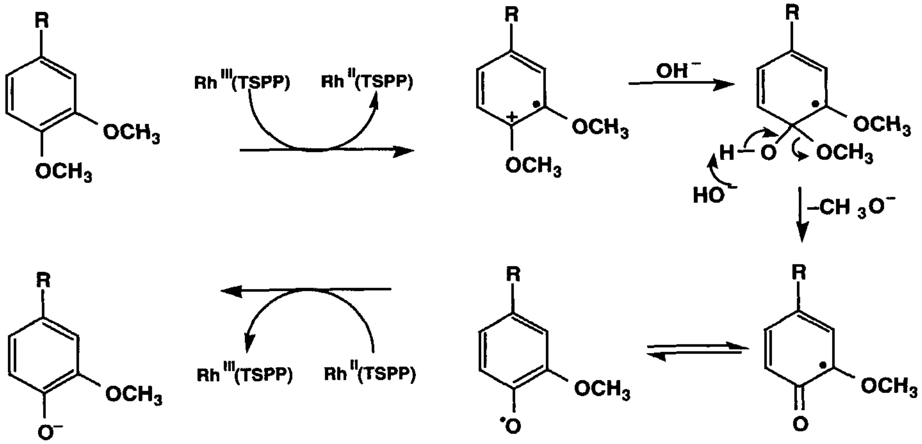
[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

Reaction Of Rh(TSPP) With The Non-phenolic Lignin Model Compound **10**

Reactions with the non-phenolic lignin model compound **10** were also investigated and the products obtained are presented in Table 3. Larger amounts of guaiacol (**2**) were formed than for the controls or the AQ catalyzed reactions, indicating the higher activity of Rh(TSPP). The most noteworthy product, however, was acetovanillone (**5**). This could only have arisen via demethylation of a methyl aryl ether bond. Demethylation of the methyl aryl ether components of lignin is an extremely important reaction as it provides a means for activating the lignin towards degradation and solubilization particularly during the bulk phase of pulping. Possible pathways by which acetovanillone (**5**) could have been formed are depicted in Scheme 3, part (a). Demethylation of any of the three methylated compounds **10**, **28**, or **29** would ultimately lead to the formation of acetovanillone (**5**) and guaiacol (**2**). However, the presence of some **29** in the overall product distribution indicates that the reaction must proceed to some extent via cleavage of the β-ether linkage in **28**. The mechanism of this particular reaction is probably the same as that proposed for **8** in Scheme 2.



SCHEME 3.
Part (a) Possible Demethylation Pathways leading to the Formation of Acetovanillone (**5**) from **10**



Part (b) Proposed Mechanism for Demethylation of Methyl Aryl Ether Lignin Model Compounds **10**, **28** and **29**

Demethylation of **10** and **28** would give **1** and **8** respectively and both of these latter compounds have been established to be sources of guaiacol (**2**) and acetovanillone (**5**) in the presence of the rhodium catalyst (see Tables 1 and 2). The relative importance of each of these demethylation pathways has not been established.

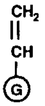
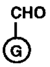
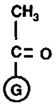
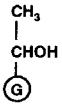
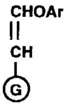
The fact that increased quantities of acetovanillone (**5**) were formed in the reaction of **10** with Rh(TSPP) in the absence of added glucose indicates that an oxidative mechanism is important for the demethylation reaction. A plausible mechanism is presented in Scheme 3, part (b). For simplicity the reduced rhodium catalyst is shown as the reductant in the last step, although other processes, such as the disproportionation of the phenoxy radical, might be important here.

Oxidative demethylation of dimethoxybenzene derivatives is a well documented reaction.[8] One electron oxidants that have been used include Mn^{3+}, Ag^{2+} and Co^{3+}.[9-11] The reaction usually proceeds to give orthoquinones from 1,2-dimethoxybenzenes if stoichiometric or excess amounts of oxidant are added and water is present in the solvent system. The reactions are postulated to proceed via radical cation intermediates. In the reactions of **10**, significant amounts of mono-demethylation was observed. This could be because the oxidant, Rh^{III}(TSPP), was only present at the 10% level. It is possible that some further demethylation and oxidation to give ortho-quinone products also occurred but was not detected because of the instability of these compounds under the conditions used.

Reactions Of Rh(TSPP) With The Phenylpropane Lignin Model Compound **11**.

Reactions of the phenylpropane lignin model compound **11** with the Rh(TSPP) catalyst were also investigated. The complete product distribution analysis is given in Table 4. Greatly increased yields of guaiacol were obtained for the rhodium catalyzed reactions compared to the controls or those catalyzed by AQ/glucose. In addition, large quantities of vanillin (**4**) were formed. Overall

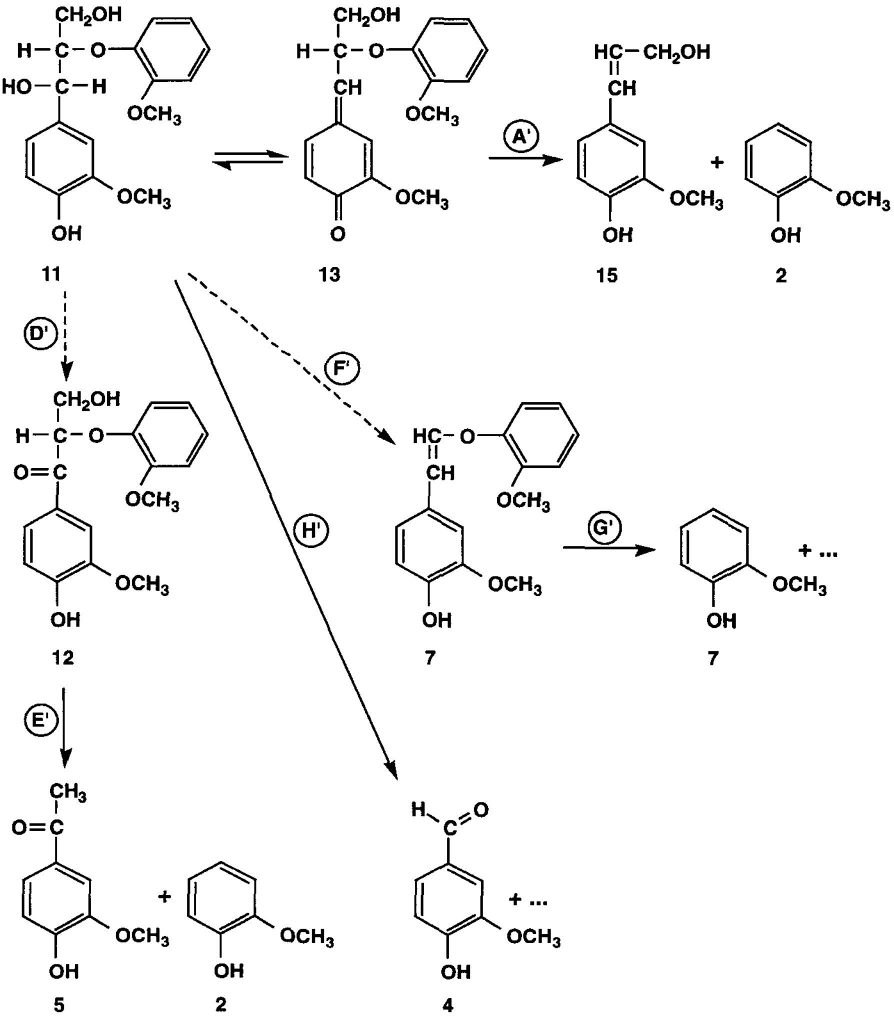
TABLE 4. Total Reaction Component Analysis for **11**[a]

						
Catalyst	%**2**	%**3**	%**4**	%**5**	%**6**	%**7**
Control	16		5			56
Control/Gl	15		2			50
AQ/Gl	43	2	6		1	22
Rh(TSPP)	74	3	40	13	1	
Rh(TSPP)/Gl	75	6	31	6	2	

[a] For definitions of symbols and reaction conditions refer to Table 1 footnote

the product distribution more closely resembled that obtained for Fe(TSPc)[5] than Co(TSPP),[4] again reflecting the importance of oxidative reactions for the rhodium catalyst.

Formation of the products obtained can be rationalized in terms of the same reaction pathways (Scheme 4) that were previously used for the Co(TSPP) and Fe(TSPc) catalysts.[4,5] The large amount of vanillin (**4**) formed suggests that pathway H' is even more important for this catalyst than it was for Fe(TSPc), especially in the absence of added glucose. The mechanism for this reaction is probably the same as that proposed for the iron catalyst.[5] The formation of significant amounts of vanillin (**4**) in the reactions to which glucose had been added indicates that **11** competes with glucose as a reductant for Rh^{III}(TSPP). The absence of any vinyl ether **7** in the products from **11** suggests that pathway F' is relatively unimportant. Although Rh(TSPP) does react with **7**, the reaction does not go to completion under the conditions used (see Table 2). Therefore, the formation of significant amounts of **7** in the reactions of **11** would result in some of this compound being detected in the products. The minor amounts of



SCHEME 4. Rationalization of the Product Distribution Obtained from Reaction of **11** with Rh(TSPP)

acetovanillone (**5**) formed suggests that pathways D' and E' are also of limited importance. In view of the large amount of guaiacol (**2**) formed and by analogy with the reactions of the other metal catalysts,[4,5] A' is probably one of the important reaction pathways leading to guaiacol (**2**) formation. We propose that pathways A' and H' are both important reaction paths for the Rh(TSPP) catalyzed reactions of **11** and that the relative importance of H' increases in the absence of glucose.

EXPERIMENTAL

The conditions for the degradation reactions, the analytical techniques used and lignin model compound preparations have been described in Part I of this series of papers.[4] Rh(TSPP)[13] and Ru(CO)(TSPP)[14] were prepared by the literature methods.

CONCLUSIONS

The catalyst Rh(TSPP) is very effective at cleaving the β-aryl ether bonds of the lignin model compounds **1**, **10** and **11** to release guaiacol (**2**). It is much more active than AQ, Co(TSPP) or Fe(TSPc), and in contrast to the first two catalysts it is equally effective both with and without added glucose. When glucose is absent, the lignin model compounds themselves probably act as reductants for Rh^{III}(TSPP). Once formed, the active, reduced form of the catalyst is then available to react with the resulting α-carbonyl products such as **8** or quinone methides such as **9**, thereby generating guaiacol (**2**). Co^{III}(TSPP) and AQ are both very ineffective catalysts in the absence of glucose.[4] This is probably because they are weaker oxidants and are therefore not capable of oxidizing the lignin model compounds; with no effective way of generating the reduced catalysts, β-ether cleavage does not readily occur. In addition, these catalysts fail to form demethylated products on reaction with 3,4-dimethoxyphenyl compounds such as **10**. This is probably a direct result of their inability to oxidize the lignin model compounds. Fe^{III}(TSPc) is able to oxidize the lignin model compounds, but it is less active than Rh^{III}(TSPP).[5]

In the presence of glucose, reactions of the reduced form of the rhodium catalyst with the quinone methides derived from the model compounds **1** and **11** increase in importance (pathways A and A' in Schemes 1 and 4 respectively). However, relatively large amounts of the oxidized products (**5** and **4** respectively) are still formed in these reactions, indicating that the lignin models compete with glucose as reductants for Rh^{III}(TSPP).

Mechanisms have been proposed for the reaction of the reduced rhodium catalyst with the α-carbonyl compound **8** and for the potentially important reaction involving demethylation of one of the methyl aryl ether groups in **10**. In both cases, it appears that single electron transfer precedes the cleavage reaction. This feature is common to the mechanisms proposed for the other important metal complex catalyzed reactions of the lignin model compounds.[4,5] The precise details of all these electron transfer processes, however, are not known and they could also vary depending on the particular reaction and catalyst. The two most likely possibilities fall under the broad headings of inner-sphere or outer-sphere electron transfer.[12] The rates are expected to be very different for these two processes and this could significantly influence the rates at which the various reactions occur.

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