

Oxidation of Phenols by Molecular Oxygen Catalysed by Transition Metal Complexes. Comparison between the Activity of Various Cobalt and Manganese Complexes and the Role of Peroxy Intermediates

Maryvonne Frostin-Rio,* Danièle Pujol, Claude Bied-Charreton, Martine Perrée-Fauvet, and Alain Gaudemer

Laboratoire de Chimie de Coordination Bioorganique, LA.255, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay Cédex, France

The oxidation reactions of hindered phenols by molecular oxygen catalysed by monomeric and polymeric cobalt-Schiff base complexes, cobalt and manganese porphyrins, and (pyridine)cobaloxime are described; the rate and selectivity of these reactions are very dependent on the catalyst and on the solvent.

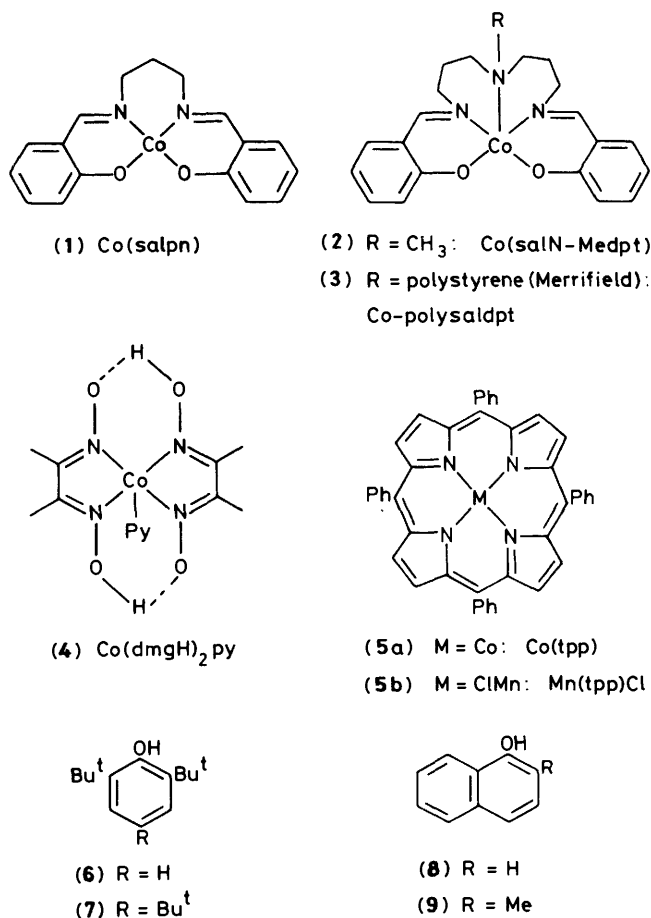
A new product has been isolated, 1,3,5-tri-*t*-butyl-4-oxocyclohexa-2,5-dienylperoxy(pyridine)cobaloxime, and was fully characterised by its elemental analysis and spectroscopic methods. The reactivity of peroxy compounds derived from 2,4,6-tri-*t*-butylphenol which are postulated as intermediates in the oxidation of this phenol has been studied. Thermal decomposition of 1,3,5-tri-*t*-butyl-4-oxocyclohexa-2,5-dienyl(pyridine)cobaloxime indicates that the formation of this complex from the phenol, O₂, and (pyridine)cobaloxime(II) is reversible and that it is converted into 2,6-di-*t*-butyl-1,4-benzoquinone only in the presence of a proton source. The corresponding hydroperoxide is probably an intermediate in this transformation as its decomposition in the presence of the cobalt(II) or manganese(III) complexes yields the same final products as the overall oxidations.

Oxidation of phenols is a relatively easy reaction which may be carried out with various oxidants.¹ However, such procedures are often non-selective, giving rise to very complex mixtures of products. Oxidation of phenols by molecular oxygen catalysed by cobalt(II) or manganese(III) complexes represents a typical example of a reaction involving the activation of dioxygen by a transition metal cation. These reactions, known since 1967,² have been the subject of numerous studies which have aimed either at optimising the experimental conditions, or at finding more efficient catalysts, or at obtaining a better knowledge of their mechanism and in particular of the role played by the metal ion. The results obtained by Nishinaga and co-workers³ and by Drago and co-workers⁴ led to a general understanding of the mechanistic features of these reactions even though convincing experimental evidence is lacking for some of the proposed steps. A thorough knowledge of the successive and/or competitive processes occurring during these oxidation reactions is necessary in order to optimise the reaction conditions and to devise new catalysts which might perform more efficiently and which would not undergo irreversible degradation during the course of oxidations.

In this paper, we report the results of a comparative study of various oxidation catalysts including monomeric and polymeric⁵ Schiff base-cobalt complexes as well as manganese and cobalt porphyrins. The results also provide new information concerning the nature of the steps which directly precede the formation of the final oxidation products from 2,4,6-tri-*t*-butylphenol in the presence of several Schiff base-cobalt complexes. Preliminary results obtained with the manganese porphyrin Mn(tpp)Cl (tpp = tetraphenylporphin) strongly suggest that this complex, like the cobalt catalysts, mediates the formation and decomposition of peroxy intermediates.

Results

(A) *Comparison of the Different Catalysts in Phenol Oxidation.*—The complexes whose catalytic activity has been investigated in phenol oxidation include the four-co-ordinate Co(salpn) complex (1) and a five-co-ordinate complex Co(salN-medpt) (2) which are both known to bind molecular oxygen at



room temperature.⁶ Among the polymeric complexes of similar structure which have been previously prepared in this laboratory,⁵ Co-polysaldpt (3), obtained by covalently binding

Table 1. Oxidation of 2,6-di-*t*-butylphenol (6)^a

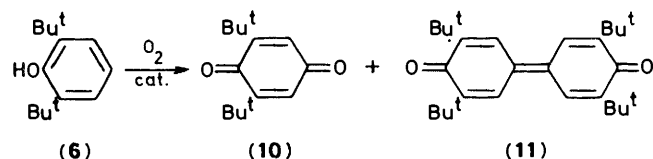
Catalyst	Solvent	Reaction time (h)	Yield (%)	(10)	(11)
Co(salpn)	CHCl ₃ or toluene	24	30	52	48
Co(salpn)	CHCl ₃ -pyridine	24	40	80	20
Co(salN-Medpt)	Toluene	6	100	100	0
Co(salN-Medpt)	CH ₃ CN	1	100	100	0
Co-polysaldpt	CHCl ₃	24	30	90	10
Co-polysaldpt	toluene	6	100	100	0
Co(dmgh) ₂ py	CH ₃ CN	24	75	100	0
Co(tpp)	CH ₃ CN	24	0		
Co(tpp)	{ CHCl ₃ or toluene or CH ₃ CN } pyridine	9	100	100	0
Mn(tpp)Cl-Bu ₄ NBH ₄	toluene	4	90	5	95
Mn(tpp)Cl-Bu ₄ NBH ₄	toluene-pyridine	4	90	0	100
Mn(tpp)Cl-Bu ₄ NBH ₄ -NaOH	toluene	4	100	34	66
Mn(tpp)Cl-NaOH	toluene	4	70	40	60
Mn(tpp)Cl-NaOH	CH ₃ CN	0.5	100	10	90

^a [Catalyst]/[Substrate] = 0.1 (cobalt complexes) or 0.01 (manganese porphyrin). [Bu₄NBH₄] or [pyridine] or [NaOH] = [Substrate].

the saldptH₂ Schiff base to a Merrifield resin followed by cobalt insertion, exhibited the most interesting characteristics in catalysis, *i.e.* insolubility, compatibility with various organic solvents (chloroform, toluene, acetonitrile), and ease of recovery. (Pyridine)cobaloxime(II), Co(dmgh)₂py (4) (dmgh = dimethylglyoximate monoanion) has already been used by Simandi and co-workers⁷ as a catalyst for the oxidation of hydroquinone. Two metalloporphyrins have been tested, namely cobalt(II) *meso*-tetraphenylporphin, Co^{II}(tpp) (5a), and chloromanganese(III) *meso*-tetraphenylporphin, Mn^{III}(tpp)Cl (5b). We have earlier reported that Co(tpp) and Mn(tpp)Cl were able to catalyse the oxidation of indolic derivatives by O₂ to the corresponding ketoamides,⁸ and that Mn(tpp)Cl catalyses the oxidation of olefins to ketones.⁹ In the former reaction, manganese porphyrin exhibits a greater activity than the cobalt complex.

Two hindered phenols frequently employed to test the efficiency of catalysts were used in this study; *viz.* 2,6-di-*t*-butylphenol (6), and 2,4,6-tri-*t*-butylphenol (7). Additional experiments were done with two naphthols whose catalytic oxidation by molecular oxygen had not been thoroughly investigated, *viz.* 1-naphthol (8) and 2-methyl-1-naphthol (9).

(1) *Oxidation of 2,6-di-*t*-butylphenol (6).* Oxidation of this phenol provides a useful test for comparing the activity of various catalysts as it can be performed with reaction times which do not generally exceed 24 h and it gives rise to only two products: 2,6-di-*t*-butyl-*p*-benzoquinone (10) and the diphenoquinone (11) (Scheme 1).

**Scheme 1.**

* Salen = bis(salicylidene)ethylenediamine.

† Oxidation of the phenol (6) may be catalysed by Mn^{III}(tpp)Cl without addition of a reducing agent or NaOH. If the reaction is run in acetonitrile, a 50% conversion into the diphenoquinone (1) is observed in 72 h, using 10% Mn(tpp)Cl (results to be published elsewhere).

As shown in Table 1, the oxidation rate is dependent on the catalyst and on the solvent. The penta-co-ordinated cobalt complexes Co(salpn)/py, Co(salN-Medpt), Co-polysaldpt, Co(dmgh)₂py, and Co(tpp)/py all catalyse the oxidation of (6) to give the quinone (10) as the major product, and in most cases as the only product, the most effective conditions being Co(salN-Medpt) in acetonitrile. With Co(saldpt) in methylene dichloride or Co(salen)* in a co-ordinating solvent (*e.g.* *NN*-dimethylformamide), Nishinaga obtained the same result.^{3f} An appreciable amount of the diphenoquinone (11) was produced only when oxidation was performed in the presence of the tetraco-ordinated Co(salpn) complex. Co^{II}(tpp) is active only in the presence of pyridine.

With Co-polysaldpt the best yields are obtained when the oxidation is carried out in toluene, probably because this polymeric complex swells much more in toluene than in chloroform. In contrast with the previous observations by Drago^{4b} using the monomeric complex (2), Co-polysaldpt (3) does not lose activity as the oxidation proceeds. The recovered polymeric catalyst could be re-employed ten times without any appreciable decrease in its catalytic efficiency.⁵

Manganese porphyrin, Mn^{III}(tpp)Cl, also catalyses the oxidation of the phenol (6) in the presence of the reducing agent Bu₄NBH₄ (1 equiv. per mol of phenol) or under basic conditions.† In both cases, the oxidations are fast, considering that there is only 1% catalyst present, and produce the diphenoquinone (11) as the major product. As with the cobalt-containing catalysts, the reaction rate is increased when it is performed in acetonitrile. The role of Bu₄NBH₄ is to reduce Mn^{III} porphyrin to Mn^{II} porphyrin which is known to bind O₂ reversibly.⁶ It should be mentioned that the oxidation of olefinic compounds could also be performed, but only in the presence of this reducing agent.⁹ Addition of NaOH provides an appreciable amount of quinone probably because it converts phenol into the more oxidizable phenolate ion. The presence of catalytic amounts of manganese porphyrin is, however, necessary to obtain a rapid oxidation of phenolate ion to products (10) and (11).

In conclusion, it is possible to obtain, by a suitable choice of the catalyst, a quantitative conversion of the phenol (6) into either the quinone (10) or the diphenoquinone (11).

(2) *Oxidation of 1-naphthol (8) and of 2-methyl-1-naphthol (9).* As shown in Table 2, not only the oxidation rate but also the selectivity of the oxidation of 1-naphthol (8) is strongly dependent on the catalyst and on the solvent. With Co(salpn)

Table 2. Oxidation of naphthols (8) and (9)^a

Naphthol	Catalyst	Solvent	Reaction time (h)	Yield (%)	Products		Other products
					(12)	(13)	
(8)	Co(salpn)	CHCl ₃	3.5	100	0		100
	Co(salN-Medpt)	CHCl ₃	3	100	50		50
	Co(salN-Medpt)	CH ₃ CN	0.5	100	100		0
	Co-polysaldpt	CH ₃ CN	24	80	50		50
	Co-polysaldpt	toluene	24	100	15		85
	Co(tpp)	CH ₃ CN-pyridine	24	85	30		70
(9)	Co(salN-Medpt)	toluene or CH ₃ CN	0.5	100		100	0
	Co-polysaldpt	toluene	0.5	100		100	0
	Co-polysaldpt	CH ₃ CN	2.5	100		100	0
	Co(tpp)	CH ₃ CN-pyridine	2.5	100		100	0
	Mn(tpp)Cl-Bu ₄ NBH ₄	CH ₃ CN	12	100		20	80

^a [Catalyst]/[Substrate] = 0.1 (cobalt complexes) or 0.01 (manganese porphyrin). [Bu₄NBH₄] or [pyridine] = [Substrate].

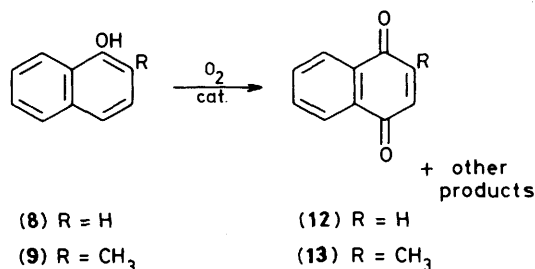
Table 3. Oxidation of 2,4,6-tri-*t*-butylphenol (7)^a

Catalyst	Solvent	Reaction time (h)	Yield (%)	Proportions				
				(10)	(14)	(15)	(16)	(17)
Co(salpn)	CHCl ₃ or toluene	24	25	25	30	13	0	32
Co(salpn)	CHCl ₃ -pyridine	24	25	32	38	25	0	5
Co(salN-Medpt)	toluene	24	30	40	7	26	20	7
Co(salN-Medpt)	CH ₃ CN	24	15	14	0	14	72	0
Co-polysaldpt	CHCl ₃ or toluene	24	15	30	35	25	0	10
Co(tpp)	toluene	24	0					
Co(tpp)	toluene-pyridine	24	55	43	21	7	0	29
Mn(tpp)Cl-Bu ₄ NBH ₄	toluene	4	100	51	0	36	0	13
Mn(tpp)Cl-Bu ₄ NBH ₄	toluene-pyridine	1	100	49	7	26	0	18
Mn(tpp)Cl-Bu ₄ NBH ₄ -NaOH or Mn(tpp)-NaOH	toluene	4	100	53	0	39	0	8
Mn(tpp)Cl-Bu ₄ NBH ₄	CH ₃ CN	1	100	51	10	33	0	6
Mn(tpp)Cl-NaOH	CH ₃ CN	0.5	100	32	29	26	0	13

^a [Catalyst]/[Substrate] = 0.1 (cobalt complexes) or 0.01 (manganese porphyrin). [Bu₄NBH₄] or [pyridine] or [NaOH] = [Substrate].

(1), oxidation is achieved in 3.5 h but does not yield the naphthoquinone (12) (Scheme 2), whereas in the presence of Co(salN-Medpt) (2) in acetonitrile a quantitative yield of quinone is obtained in 0.5 h, chloroform being a less suitable solvent. The polymeric complex Co-polysaldpt (3) is much less efficient and considerably less selective than the corresponding monomeric catalyst. A variety of other unidentified products is formed in addition to the naphthoquinone (12). These products were difficult to identify but might be dimeric products due to oxidative coupling of phenoxy radicals, according to the elemental analysis and spectroscopic data.*

In contrast, the oxidations of 2-methyl-1-naphthol (9) are very fast and specific, as the only oxidation product, obtained in quantitative yield, is the 2-methylnaphthoquinone (13). The nature of the solvent does not affect the reaction and, surprisingly, the polymeric complex (3) was also found to

**Scheme 2.**

be an efficient catalyst for this oxidation. Attempts to oxidise 1-naphthol in the presence of Mn(tpp)Cl were unsuccessful. However, oxidation of 2-methyl-1-naphthol with the Mn(tpp)Cl-Bu₄NBH₄ catalytic system provides a mixture of 2-methylnaphthoquinone (13) (20%) and other products which were difficult to identify.

(3) *Oxidation of 2,4,6-tri-*t*-butylphenol (7)*. Compared with the oxidation of 2,6-di-*t*-butylphenol (6), oxidation of the phenol (7) is generally slower and provides a more complex mixture of products (Scheme 3). Results are given in Table 3. With both monomeric Schiff base-cobalt complexes, only 25% of this phenol was oxidised after 24 h. Besides *para*-oxidation products, n.m.r. spectra show that, in some cases, oxidation occurs at the *ortho* position but the amount of products resulting from *ortho*-oxidation never exceed 15%. Except for the peroxide (15), all the oxidation products have already been described by Nishinaga and his co-workers.³ The structure of peroxide (15) has been unambiguously established by its spectroscopic data and elemental analysis (see Experimental section).

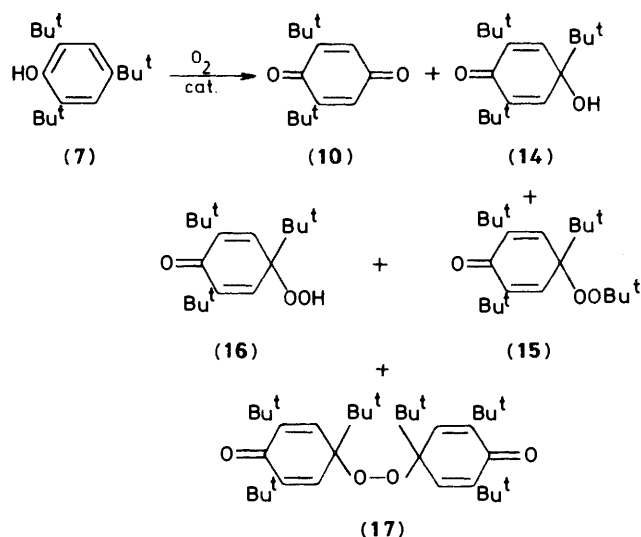
Using the cobalt complexes as catalysts, the yields of the various oxidation products varied with the catalyst and the

* Complete transformation of the starting material was observed and, besides identified quinone, a black powder giving a purple solution was isolated (Found: C, 83.8; H, 4.5. Coupling product C₂₀H₁₂O₂ requires C, 84.5; H, 4.22%; *m/z* (chemical ionization/desorption) (reagent gas NH₃) 285 (*M* + 1, 7%) and 302 (*M* + 18, 3.1). The i.r. spectrum shows two absorptions at 1 650 and 1 660 cm⁻¹ which can be attributable to a diphenoquinone system.

Table 4. Decomposition of 1,3,5-tri-*t*-butyl-4-oxocyclohexa-2,5-dienylperoxy(pyridine)cobaloxime (**18a**)
(18a) \longrightarrow 2,4,6-tri-*t*-butylphenol (**7**) + 2,6-di-*t*-butyl-*p*-benzoquinone (**10**)

Experimental conditions	Products (%)		
	(7)	(10)	(18a)
Under N ₂ or pressure of O ₂ ^a in refluxing toluene or dioxane	95	5	
Under pressure of O ₂ in refluxing dioxane-water mixture (80:20)	85	15	
Under N ₂ or air in toluene at 50 °C	100		
Under pressure of O ₂ in toluene at 50 °C	40	27	33
Under pressure of O ₂ in dioxane at 50 °C	80	20	
Under pressure of O ₂ in dioxane-water mixture (80:20) at 50 °C	65	35	
Chromatography on an acidic silica gel column	50	50	
1 equiv. CF ₃ CO ₂ H in CDCl ₃ at room temperature			100

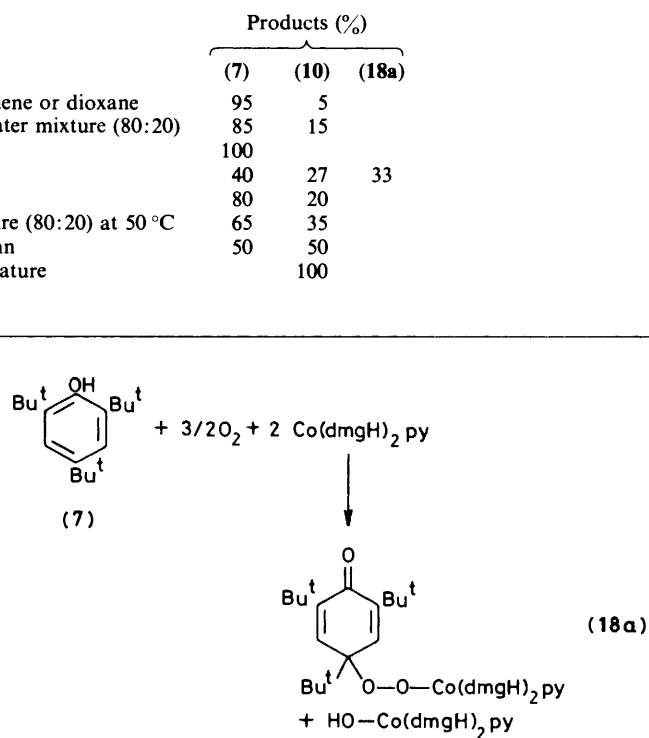
^a Pressure of O₂ = 200 mmHg.



Scheme 3.

solvent but not as much as in the oxidation of the 2,6-di-*t*-butylphenol (**6**). A reasonable explanation for the formation of these products is given in part B which presents a mechanistic study of these oxidations. As with the oxidation of the phenol (**6**), the relative amount of dimeric oxidation product (**17**) increases when going from five-co-ordinate to four-co-ordinate cobalt-Schiff base complexes. With Co(salN-Medpt) (**2**) in acetonitrile, the oxidation rate is slower and the hydroperoxide (**16**) is the major product. The best yields in the oxidation products were obtained with Co(tpp)/py. (Pyridine)cobaloxime(II) is not active as a catalyst in the oxidation of the phenol (**7**), as it reacts with (**7**) in the presence of O₂ to provide, quantitatively, 1,3,5-tri-*t*-butyl-4-oxocyclohexa-2,5-dienylperoxy(pyridine)cobaloxime (**18a**) (Scheme 4). Nishinaga and his co-workers³ previously observed the formation of similar peroxy complexes during the oxygenation of 2,4,6-tri-*t*-butylphenol in the presence of five-co-ordinate cobalt(II)-Schiff base complexes.

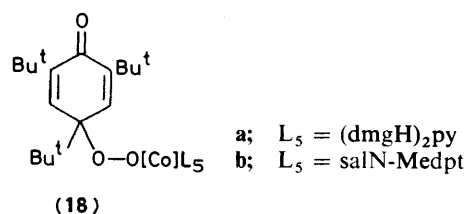
In the presence of a reducing agent or NaOH, the manganese porphyrin Mn(tpp)Cl is a more efficient catalyst for the oxidation of (**7**) than the cobalt complexes.* Complete oxidations were obtained in 4 h, the pyridine adduct catalysing the reaction even more efficiently. The reaction rate is also



Scheme 4.

dependent on the solvent and is greatly increased in acetonitrile. When the oxidations are carried out in toluene, the quinone (**10**) and the peroxide (**15**) are the two major products. In acetonitrile, an appreciable amount of the quinol (**14**) is formed, reducing the yields of the other two products.

(B) *Mechanism of the Reaction.*—Our longstanding interest both in oxidation reactions with O₂ catalysed by cobalt and manganese complexes^{8,9} and in the chemistry of peroxy complexes of cobalt¹⁰ led us to re-examine the role played by these metals in phenol oxidations. The variety of reaction products formed during the oxidation of 2,4,6-tri-*t*-butylphenol (**7**) by O₂, as shown in Table 3, makes this reaction quite suitable for a mechanistic study; furthermore it is possible to prepare independently some of the postulated intermediates: the peroxy complex (**18**) and the hydroperoxide (**16**) which is one of the major products formed in the presence of Co(salN-Medpt). We have been concerned with a study of the chemical reactivity of both compounds (**16**) and (**18a**) under various experimental conditions.



* Oxidation of the phenol (**7**) may be catalysed by 10% Mn(tpp)Cl without Bu₄NBH₄ or NaOH, either in toluene or in acetonitrile; the oxidation is quantitative in 72 h (results to be published later).

(1) *Thermal and acid-catalysed decomposition of 1,3,5-tri-*t*-butyl-4-oxocyclohexa-2,5-dienylperoxy(pyridine)cobaloxime (18a).* As mentioned before, (pyridine)cobaloxime(II) is a very

Table 5. Decomposition of hydroperoxide (16) in the presence of cobalt and manganese complexes

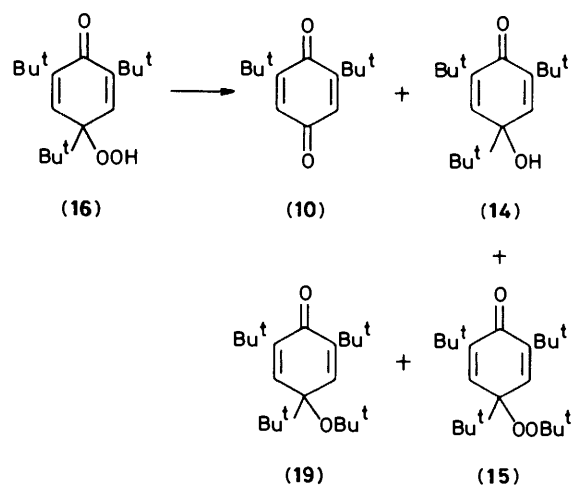
Complex	Solvent	[Complex]/ [(16)]	Reaction time (h)	Percentage decomposition (%)	Proportions			
					(10)	(14)	(15)	(19)
Co(salpn)	CHCl ₃	1	24	100	43	36	21	0
	CHCl ₃	0.25	24	100	46	16	38	0
	CHCl ₃	0.1	24	100	47	21	32	0
Co(salN-Medpt)	toluene	1	24	100	45	14	41	0
	CHCl ₃	1	24	85	59	20	Trace	21
	CHCl ₃	0.1	24	100	50	15	35	Trace
	toluene	1	24	90	57	21	Trace	22
Co-polysaldpt	toluene	0.1	24	100	48	19	33	Trace
	toluene	0.1	24	100	45	25	30	Trace
Co(dmgH) ₂ py	CHCl ₃	1	24	100	82	9	0	9
	CH ₃ CN	1	24	100	76	12	12	Trace
	CH ₃ CN	0.1	24	100	65	23	12	Trace
Mn(tpp)Cl	toluene	0.01	4	100	51	11	38	0
	CH ₃ CN	0.01	1	100	54	11	35	0

selective catalyst for the oxidation of 2,6-di-*t*-butylphenol (Table 1) but with phenol (7) the same complex, in the presence of oxygen, leads to the stable peroxy complex (18a) (Scheme 4): the remarkable stability of (18a) prevents the oxidation from going further and precludes (pyridine)cobaloxime from acting as a catalyst. However, decomposition of complex (18a) may be achieved, either thermally in 4 h in neutral solution or at room temperature in acidic medium. The results are given in Table 4. They unambiguously show that decomposition of (18a) in toluene under nitrogen or air does not give rise to detectable amounts of the quinone (10). The only organic product obtained, in nearly quantitative yield, is 2,4,6-tri-*t*-butylphenol (7). When the decomposition is carried out under pressure of oxygen, (18a) is partially decomposed into quinone but the phenol (7) remains as the main product; addition of water to the reaction mixture increases the amount of quinone formed. On the other hand, acidic treatment of complex (18a) leads to the rapid and exclusive formation of the quinone.

Two important conclusions can be drawn from these results. (1) The formation of complex (18a) from (pyridine)cobaloxime(II), O₂, and the phenol (7) is a reversible reaction. Drago *et al.*,^{4b} on the basis of e.s.r. experiments, came to a similar conclusion concerning complex (18b) with the Schiff base SalN-Medpt as the equatorial ligand. (2) In the absence of a proton source (acid or water) and oxygen, decomposition of complex (18a) gives very little quinone. In contrast, the easy and quantitative conversion of (18a) into the quinone (10) under acidic conditions suggests that the hydroperoxide (16) is an intermediate in this reaction and that it is the direct precursor of the quinone. It has previously been shown that acidic treatment of alkylperoxycobaloximes leads to carbonyl derivatives *via* the corresponding hydroperoxide.^{10c} These results led us to investigate the decomposition of hydroperoxide (16) in the presence of the same cobalt or manganese catalysts.

(2) *Decomposition of hydroperoxide (16) in the presence of cobalt(II) and manganese(III) complexes.* Hydroperoxide (16) was prepared by the method described by Nishinaga *et al.*¹¹ and was then decomposed in the presence of stoichiometric or catalytic amounts of the complexes Co(salpn), Co(salN-Medpt), Co-polysaldpt, (pyridine)cobaloxime(II), and Mn(tpp)Cl under the same experimental conditions as the phenol oxidation. The results are shown in Table 5. Whatever the complex, decomposition of hydroperoxide (16) leads to a mixture of three products: the quinone (10) and quinol (14) with either the *t*-butyl peroxide (15) or the *t*-butyl ether (19) (Scheme 5).

With all the cobalt complexes, the quinone is the major



Scheme 5.

product with yields ranging from 43–47% [Co(salpn)] to 65–82% [cobaloxime(II)]. The phenol (7) was never detected which suggests that, under these conditions, the hydroperoxide (16) and the cobalt(II) complex are not in equilibrium with the peroxycobalt complex (18).

Compounds (10), (14), and (15) are also products of the oxidation of the phenol (7) by O₂ catalysed by Co(salpn), Co(salN-Medpt), or Co-polysaldpt (Scheme 3). It thus appears quite likely that hydroperoxide (16) is an intermediate during these oxidations.

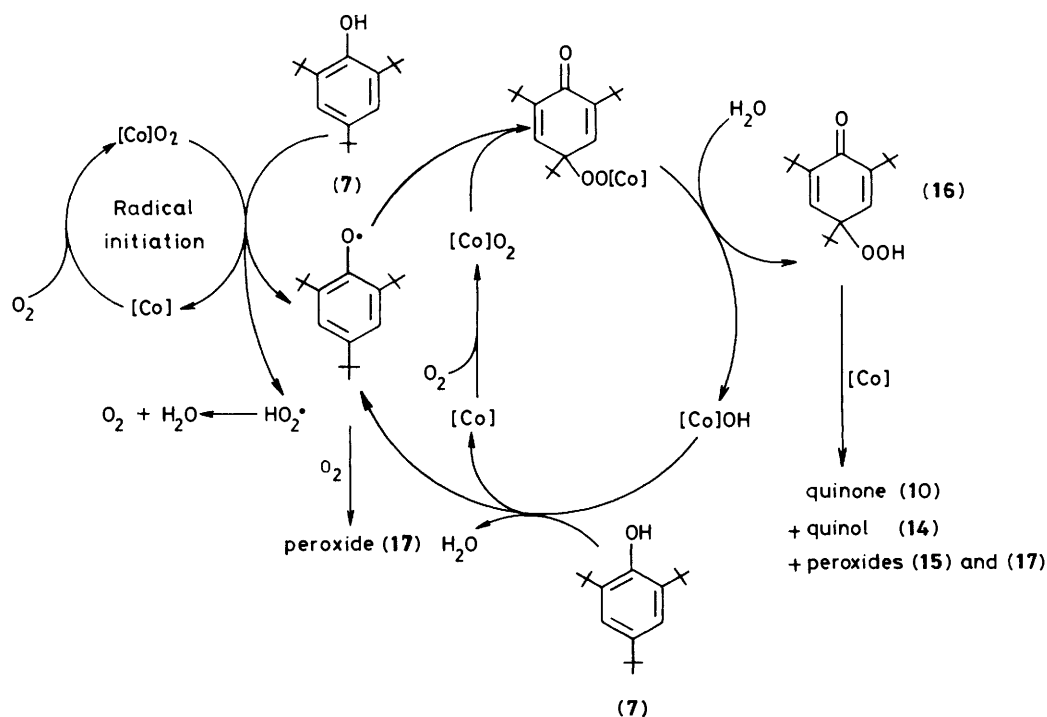
The decomposition of hydroperoxide (16) is also catalysed by Mn(tpp)Cl, without addition of the reducing agent (Table 5), at rates which are as high or higher than the rate of the overall oxidation. In acetonitrile, the products of this decomposition and their relative percentages are identical with those of the oxidation reaction, while in toluene, some quinol (14) is formed which did not appear in the overall reaction.

(3) *Oxidation of the phenol (7) in the presence of cobalt or manganese complexes and dehydrating agents.* If the above assumption is correct, namely that hydroperoxide (16) is an intermediate, then water, whether present in the reaction solvents or formed during the oxidation, must play a crucial role as it is necessary in order to transform the complex (18) into the much less stable hydroperoxide. By running the reaction in the presence of a dehydrating agent, namely a molecular sieve or

Table 6. Influence of the addition of a dehydrating agent on the oxidation of phenols

Phenol	Catalyst	Solvent	[Catalyst]/ [Phenol]	Reaction time (h)	Yield (%)	Proportions						
						(10)	(11)	(14)	(15)	(16)	(17)	
	Co(dmgh) ₂ py	CH ₃ CN	1	1	100	100						
		CH ₃ CN + sieve	1	1	100							
	Co(dmgh) ₂ py	CH ₃ CN	0.1	24	75	100						
		CH ₃ CN + sieve	0.1	24	35	100						
	Co-polysaldpt	CHCl ₃	0.07	24	20	85	15					
		CHCl ₃ + sieve	0.07	24	12	85	15					
		CHCl ₃ + DMP ^a	0.07	24	10	85	15					
	Co(salpn)	CHCl ₃	1	24	100	25			31	19	0	25
		CHCl ₃ + sieve	1	24	35	30			20	20	0	30
		CHCl ₃ + DMP	1	24	27	45			20	15	0	20
	Co(salpn)	CHCl ₃	0.1	24	25	25			30	13	0	32
		CHCl ₃ + sieve	0.1	24	0							
		CHCl ₃ + DMP	0.1	24	0							
	Mn(tp)Cl-Bu ₄ NBH ₄	toluene	0.01	4	100	51			0	36	0	13
		toluene + sieve	0.01	72	40	50			3	36	0	11

^a DMP = 2,2-dimethoxypropane. [DMP] = [phenol].



Scheme 6.

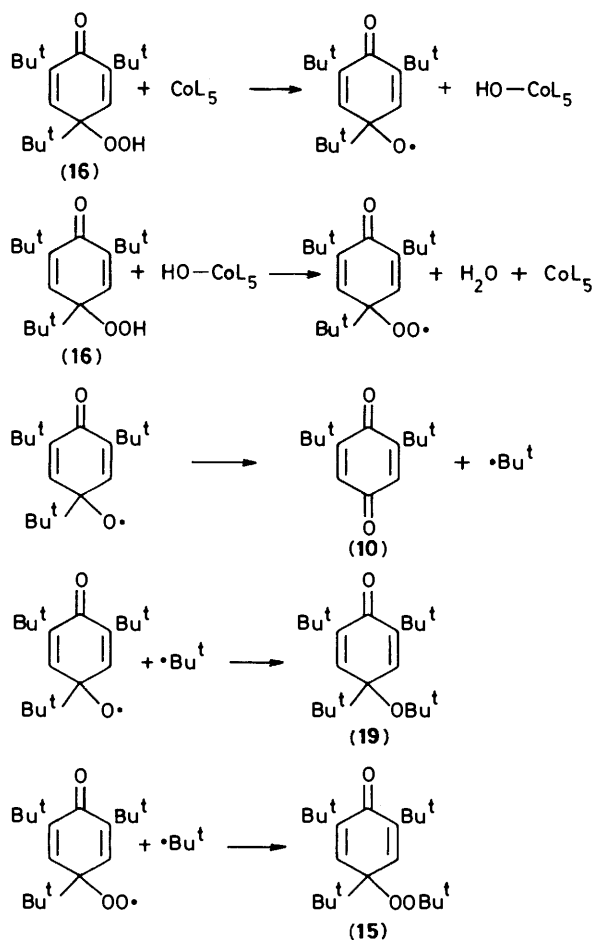
2,2-dimethoxypropane,¹² one should hinder this conversion and slow down the oxidation reaction. The results of the relevant experiments, carried out in the presence of both stoichiometric and catalytic amounts of catalyst, are shown in Table 6. Addition of a molecular sieve or 2,2-dimethoxypropane to the reaction mixture produces an important decrease in the reaction rate, both for the phenol (7) and 2,6-di-*t*-butylphenol (6). However, no effect was observed under conditions giving a fast reaction [using a stoichiometric amount of Co(dmgh)₂py]. It is reasonable to assume that, in this case, all steps, including the hydrolysis of complex (18) to (16), are more rapid than the trapping of water by the sieve, whereas if the overall reaction is slower, the hydrolysis step may be rate-limiting.

Discussion

The comparative study of the catalytic activities of various cobalt-Schiff base complexes and Co^{II} and Mn^{III} porphyrins in the oxidation of phenols shows that reaction rates and selectivities of oxidation are largely dependent on the nature of the catalyst and on the solvent. With 2,6-di-*t*-butylphenol (6), 1-naphthol (8), and 2-methyl-1-naphthol (9), the best yields in quinones and the highest reaction rates were obtained with Co(salN-Medpt) (2) in acetonitrile. The polymeric Co-polysaldpt, although less reactive than the monomeric analogue, exhibits very high selectivity and a greater stability. This catalyst may consequently be very useful when large amounts of oxidation products are required or when the recovery of the catalyst is important.

The detailed study of oxidation of 2,4,6-tri-*t*-butylphenol and of the reactivity of the postulated peroxy intermediates allows us to give a more precise description of some of the steps leading from the phenol (7) to the final oxidation products. A possible mechanism for the cobalt(II)-catalysed oxidation taking into account the experimental results obtained by Nishinaga,³ and Drago,⁴ and ourselves is shown in Scheme 6. In this sequence of reactions, cobalt complexes appear to be involved in five steps. (1) Formation of an oxygen-adduct which can abstract a hydrogen atom from the phenol to give a phenoxyl radical. (2) The same oxygen-adduct can react reversibly with the phenoxyl radical to give the peroxy complex. (3) Hydrolysis of this complex leads to hydroperoxide (16) and to the complex HO-CoL₅. (4) This complex oxidises the phenol (7) to the phenoxyl radical, re-forming the starting cobalt(II) complex: this step is essential to return the metal to its divalent state. (5) The hydroperoxide (16), in the presence of the cobalt complex, decomposes to the final oxidation products. Strong experimental evidence has been obtained for all these reactions, except step (4).*

The mechanism of step (5) is not known in detail but



* Preliminary experiments carried out in our laboratory indicate that Co^{III}(salN-Medpt)OH complex also catalyses the oxidation of phenols by O₂. Nishinaga studied the oxygenation of 2,6-di-*t*-butyl-4-methylphenol in the presence of an equimolar amount of Co^{III}(saldpt)OH in CH₂Cl₂ at 0 °C and 1-methyl-4-oxo-3,5-di-*t*-butylcyclohexa-2,5-dienylperoxycobalt(III) (saldpt) (18b) in quantitative yield.^{3g}

reasonable explanations can be put forward based on the well known decomposition of hydroperoxides catalysed by transition metal salts.¹³ Similar processes can be involved here (Scheme 7). Quinone (10) and ether (19) probably arise from the quinoxyl radical which is produced by direct decomposition of the hydroperoxide (16). The peroxide (15) is most likely formed from the peroxy radical which may be produced by a redox reaction between the hydroperoxide and the complex HO-CoL₅, though its formation during the overall oxidation might also be explained by a coupling reaction of the phenoxyl and *t*-butylperoxy radicals.† Formation of the quinol (14) is not so easy to rationalise: we checked that this product is stable under the reaction conditions and that it is not an intermediate in the formation of the other oxidation products. It appears reasonable to assume that the quinol is produced by the reduction of the hydroperoxide by the cobalt(II) complex itself. As for the coupling product (17), it is probably formed by reaction of the phenoxyl radicals not only with oxygen, but also with the peroxy radical formed during the decomposition of the hydroperoxide. Further experiments will be performed in order to verify these assumptions.

It should be emphasised that this mechanistic scheme is valid only for the oxidation of 2,4,6-tri-*t*-butylphenol. However, even if experimental evidence is lacking for an extension of this mechanism to the reactions of other phenols, it seems reasonable to postulate that their oxidation follows the same general pattern. The greater selectivity observed in the oxidation of 2,6-di-*t*-butylphenol can be easily explained by the fact that the quinone can be formed both from the quinoxyl radical and from the corresponding quinol, which must be a readily oxidisable intermediate.

Experimental

Materials and Methods.—All solvents and starting phenols were reagent-grade and used without further purification.

The monomeric complexes Co(salpn) (1) and Co(salN-Medpt) (2) were prepared according to the published procedures.¹⁴ The synthesis of polymeric cobalt-Schiff-base complexes has been described previously.⁵ Co-polysaldpt (3) was prepared from Merrifield polymer Biobeads SX1 and contained 0.5 mol equiv. of cobalt per gram. (Pyridine)cobaloxime (4) was prepared by Schrauzer's method¹⁵ and the metalloporphyrins Co(tpp) (5a) and Mn(tpp)Cl (5b) were synthesised according to the method of Adler.¹⁶

I.r. spectra were recorded on a Beckman Acculab 10 spectrophotometer (in KBr pellets or as a film on NaCl plates), ¹H n.m.r. spectra on a Perkin-Elmer R-32 spectrometer using CDCl₃ solutions and SiMe₄ as internal reference, and mass spectra on a Ribermag R-10 instrument.

General Procedure for the Oxidation of Phenols.—To a solution of the starting phenol (10.1M) in the appropriate solvent was added the catalyst [Co-complex (0.01M) or Mn-porphyrin (0.001M)]. The solution was stirred in a two-necked flask connected to a gas-burette oxygen (pressure 1.2 atm) and the oxygen consumption was measured under constant pressure (1 atm) at regular intervals. At the end of the reaction, the solvent was evaporated off under reduced pressure and the different products were separated by chromatography on a silica gel column (Merck CC7) eluted with hexane containing increasing percentages of methylene dichloride; with the polymeric complex, the catalyst was removed by filtration. The organic compounds were characterised by comparison of their properties with those described in the literature. The

† We thank a referee for pointing out this possibility to us.

Table 7. Spectroscopic data of oxidation products

Product	δ_{H}					$\nu_{\text{max.}}(\text{cm}^{-1})$
	Bu ¹		C=CH	OOH	dmg	
(10)	1.3		6.5			1 650s
(11)	1.35		7.72			1 600s, 1 635m
(12)			6.98			1 630s, 1 570s
(13)			6.85 (d)		2.18 (d)	1 660s, 1 575s
(14)	1.22	0.95	6.6			1 645m, 1 665s, 3 600
(15)	1.22	1.18	6.7			1 650s, 1 670m, 890
(16)	1.23	0.95	6.72	8.3		1 650s, 1 670s, 885, 3 600
(17)	1.28	0.85	6.7			1 640m, 1 660m, 890
(18a)	1.22	0.75	6.6		2.24	1 630s, 1 650m, 890

spectroscopic data of the various products are collected in Table 7. The peroxide (15) was purified using h.p.l.c. under the following conditions: solvent methylene dichloride-hexane (30:70); column ultrasphere Si (1:25 cm, *d* 1 cm); pressure 2 000 p.s.i. (Found: C, 75.3; H, 10.9. C₂₂H₃₈O₃ requires C, 75.43; H, 10.86%); *m/z* [chemical ionization/desorption (reagent gas NH₃)] 351 (*M* + 1, 4.5%), 368 (*M* + 18, 7), 278 (*M* - OBU¹ + 1, 100), and 295 (*M* - OBU¹ + 18, 7).

*Synthesis of 1,3,5-Tri-*t*-butyl-4-oxocyclohexa-2,5-dienyl(pyridine)cobaloxime (18a).*—Oxygen was bubbled through a solution of 2,4,6-tri-*t*-butylphenol (7) (2 mmol) and Co(dmgH)₂py (4 mmol) in acetonitrile (20 ml) and the mixture was stirred at room temperature for 4 h. The cobalt complex (18a) precipitated and was obtained by filtration as a green powder, yield 95% (Found: C, 55.9; N, 10.85; Co, 9.05. C₃₁H₄₈CoN₂O₇ requires C, 56.28; N, 10.59; Co, 8.92%). Spectroscopic data for this compound are reported in Table 7.

*Decomposition of 1,3,5-Tri-*t*-butyl-4-oxocyclohexa-2,5-dienyl(pyridine)cobaloxime (18a).*—(A) *Thermal decomposition.* A solution of (18a) was stirred for 4 h at various temperatures and solvents under nitrogen or oxygen as described in Table 4. At the end of each decomposition reaction the brown precipitate formed was filtered off, the solvent was evaporated under reduced pressure, and the crude reaction product was analysed by n.m.r. spectroscopy.

(B) *Acid-catalysed decomposition. Alternative Procedures.* (i) The alkyl peroxy-cobaloxime (18a) (0.2 mmol) was dissolved in the minimum volume of CH₂Cl₂ and chromatographed on an acidic silica gel column (Merck, CC4) using the same solvent for elution. Evaporation of the eluate under reduced pressure gave a mixture of the phenol (7) (0.1 mmol) and quinone (10) (0.1 mmol), whereas the cobalt complex remained at the top of the column as a brown product.

(ii) The alkyl peroxy-cobaloxime (18a) (0.05 mmol) was dissolved in CDCl₃ (0.5 ml) containing CF₃CO₂H (0.05 mmol); the green colour immediately changed to brown and the solution was examined by n.m.r. spectroscopy: the spectrum revealed the formation of quinone (10) besides a (pyridine)cobaloxime(III) complex.

Decomposition of Hydroperoxide (16) in the Presence of Cobalt or Manganese Complexes.—Hydroperoxide (16) was synthesised by the method of Nishinaga.¹¹ To a solution of this compound (0.5 mmol) in the appropriate solvent (5 ml) was added the catalyst. The mixture was stirred at room temperature, the reaction time varying with the catalyst (Table 5). The solvent was evaporated off and the organic products

were separated from the complex by chromatography on a silica gel column and analysed by n.m.r. spectroscopy: besides products (10) (14), and (15), which were previously mentioned (Table 3), the *t*-butyl ether (19) was also found in two experiments. Compound (19) had been isolated and characterised by Nishinaga *et al.*^{3f} in a similar reaction: $\delta(\text{CDCl}_3)$ 0.9 (9 H, s), 1.17 (9 H, s), 1.23 (18 H, s), and 6.72 (2 H, s).

Influence of the Addition of a Dehydrating Agent on the Oxidation of Phenols.—The general procedure for the oxidation of phenols has been used under anhydrous conditions. A dehydration agent, either molecular sieves (Merck, 4 Å) or 2,2-dimethoxypropane, was added to the mixture to trap water eventually formed during the oxidation reaction.

Control Experiments.—Each phenol was stirred in toluene solution under one atmosphere of oxygen for 4 d. No absorption of oxygen was observed and the starting phenol was recovered in quantitative yield.

Acknowledgements

We thank Mrs. K. N. V. Duong for fruitful discussions and Mrs. F. Gaudemer for technical assistance with h.p.l.c.

References

- M. L. J. Mihailovic and Z. Cekovic, 'Oxidation and Reduction of Phenols,' in 'The Chemistry of the Hydroxy group,' ed. S. Patai, Interscience, 1971, vol. I, p. 505; D. A. Whiting, 'The Oxidation of Phenols,' in 'Comprehensive Organic Chemistry,' ed. J. F. Stoddart, Pergamon, London, 1979, vol. I, p. 739; D. G. Lee and C. F. Sebastian, *Can. J. Chem.*, 1981, **59**, 2776, 2780.
- H. M. Van Dort and H. J. Geursen, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 520; D. L. Tomaja, L. H. Vogt, jun., and J. G. Wirth, *J. Org. Chem.*, 1970, **35**, 2029; A. McKillop and S. J. Ray, *Synthesis*, 1977, 847; T. J. Fullerton and S. P. Ahern, *Tetrahedron Lett.*, 1976, 139; S. A. Bedell and A. E. Martell, *Inorg. Chem.*, 1983, **22**, 364; A. E. Martell, *Pure Appl. Chem.*, 1983, **55**, 125.
- (a) T. Matsuura, K. Watanabe, and A. Nishinaga, *J. Chem. Soc., Chem. Commun.*, 1970, 163; (b) A. Nishinaga, K. Nishizawa, H. Tomita, and T. Matsuura, *J. Am. Chem. Soc.*, 1977, **99**, 1287; (c) A. Nishinaga, K. Watanabe, and T. Matsuura, *Tetrahedron Lett.*, 1974, 1291; A. Nishinaga, H. Tomita, and T. Matsuura, (d) *ibid.*, 1979, p. 2893; (e) *ibid.*, 1980, **21**, 1261; (f) A. Nishinaga and H. Tomita, *J. Mol. Catal.*, 1980, **7**, 179; (g) A. Nishinaga, H. Tomita, K. Nishizawa, and T. Matsuura, *J. Chem. Soc., Dalton Trans.*, 1981, 1504.
- (a) R. S. Drago, J. Gaul, A. Zombeck, and D. K. Straub, *J. Am. Chem. Soc.*, 1980, **102**, 1033; (b) A. Zombeck, R. S. Drago, B. B. Corden, and J. H. Gaul, *ibid.*, 1981, **103**, 7580.
- C. Bied-Charreton, M. Frostin-Rio, D. Pujol, A. Gaudemer, R. Audebert, and J. P. Idoux, *J. Mol. Catal.*, 1982, **16**, 335.

- 6 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139.
- 7 S. Nemeth, Z. Szeverenyi, and L. I. Simandi, *Inorg. Chim. Acta*, 1980, **44**, L107.
- 8 M. N. Dufour, A. L. Crumbliss, G. Johnston, and A. Gaudemer, *J. Mol. Catal.*, 1980, **7**, 277.
- 9 M. Perrée-Fauvet and A. Gaudemer, *J. Chem. Soc., Chem. Commun.*, 1981, 874.
- 10 (a) C. Fontaine, K. N. V. Duong, C. Merienne, A. Gaudemer, and C. Gianotti, *J. Organomet. Chem.*, 1972, **38**, 167; C. Bied-Charreton and A. Gaudemer, (b) *J. Am. Chem. Soc.*, 1976, **98**, 3997; (c) *Tetrahedron Lett.*, 1976, 4153; (d) *J. Organomet. Chem.*, 1977, **124**, 299; (e) J. Deniau and A. Gaudemer, *ibid.*, 1980, **191**, C1; (f) M. Perrée-Fauvet and A. Gaudemer, *ibid.*, 1976, **120**, 439.
- 11 A. Nishinaga, T. Shimizu, and T. Matsuura, *J. Org. Chem.*, 1979, **44**, 2983.
- 12 H. Mimoun, M. M. Perez Machirant, and I. Sérée de Roch, *J. Am. Chem. Soc.*, 1978, **100**, 5437.
- 13 (a) J. K. Kochi, *J. Am. Chem. Soc.*, 1963, **85**, 1958; (b) R. Hiatt, K. C. Irwin, and C. W. Gould, *J. Org. Chem.*, 1968, **33**, 1430; (c) K. W. Lee and J. San Filipino, jun., *ibid.*, 1983, **48**, 259; (d) N. S. Enikolopyan, K. A. Bogdanova, and K. A. Askarov, *Russ. Chem. Rev. (Engl. Transl.)*, 1983, **52**, 13; (e) T. A. Dix and L. J. Marnett, *J. Am. Chem. Soc.*, 1983, **105**, 7001.
- 14 R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, 1947, **69**, 1886.
- 15 G. N. Schrauzer and Lian Pin Lee, *J. Am. Chem. Soc.*, 1970, **92**, 1551.
- 16 A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.

Received 11th October 1983; Paper 3/1798