

Homogeneous Catalytic Oxidation of Carbon Monoxide and Ketones with Oxygen in the Presence of Complexes of Rhodium(0), Iridium(I), and Platinum(0)¹

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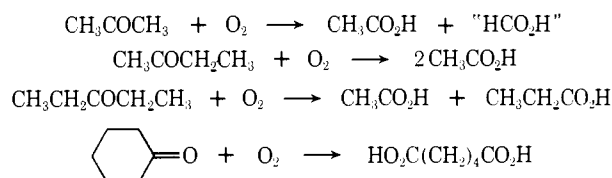
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Abstract: The compound $\text{Rh}_6(\text{CO})_{16}$ is an effective catalyst for the oxidation of CO to CO_2 with molecular oxygen under conditions of elevated temperature and pressure. When acetone is used as solvent the ketone is oxidized to acetic acid. The complexes $\text{Rh}_6(\text{CO})_{16}$, $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, and $\text{Pt}(\text{PPh}_3)_3$ can be used for the oxidation of 2-butanone, cyclohexanone, and 3-pentanone to acetic acid, adipic acid, and a mixture of acetic and propionic acids, respectively. The mechanism is a free-radical autoxidation. Acetophenone is not oxidized. Oxidation of cyclohexanone in the presence of methanol or ethanol yields dimethyl and diethyl adipate, respectively.

In a preliminary communication we have reported that the compound $\text{Rh}_6(\text{CO})_{16}$ is an effective homogeneous catalyst for the oxidation, with molecular oxygen, both of carbon monoxide to carbon dioxide, and of aliphatic ketones to carboxylic acid.² Little mechanistic information was presented in that article, although it was tacitly assumed that a transition metal oxygen complex was likely involved. We have now extended the work to platinum metal complexes which readily form oxygen complexes, and discovered that the catalytic oxidation of aliphatic ketones with oxygen is also observed with the compounds $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Pt}(\text{PPh}_3)_3$. Since the publication of our initial communication other workers have reported that these latter compounds are effective catalysts for the oxidation of benzaldehyde with molecular oxygen.³ These low valent platinum metal complexes have also been used in the oxidation of alkenes,⁴ tertiary phosphines,⁵ and isocyanides.⁶ Ketones, however, undergo oxidation only with considerable difficulty, and the literature on their conversion to carboxylic acids is rather sparse. In this paper we describe the scope and limitations of using these transition metal complexes for the oxidation of ketones to carboxylic acids, and discuss some of the salient mechanistic features of the reaction.

Results and Discussion

In a preliminary communication we reported that the oxidation of carbon monoxide to carbon dioxide occurs in the presence of $\text{Rh}_6(\text{CO})_{16}$ as catalyst at temperatures of 80 °C or greater, when a stoichiometric ratio of carbon monoxide and oxygen is present at a pressure of 15–20 atm. When acetone is used as solvent for this oxidation there is a partial oxidation of this solvent to acetic acid.⁷ Interestingly, when the complexes $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Pt}(\text{PPh}_3)_3$ are heated at 100 °C in acetone solution under a pressure of 15–20 atm of oxygen, oxidation to acetic acid does not occur. Nevertheless, under similar conditions these compounds are effective for the catalytic oxidation of 2-butanone, 3-pentanone, and cyclohexanone. The respective products from these oxidations are acetic acid, an equimolar amount of acetic and propionic acids, and adipic acid. Acid identification has been carried out by gas chromatography for the monobasic acid. In the case of adipic acid the material has been isolated as a pure compound and characterized both by its melting point and the mass spectra of its methyl and ethyl esters. These results show that the ketone suffers carbon-carbon bond cleavage at the keto carbon with oxidation of both the alkyl and acyl groups to carboxyl functions. The results show that oxidation of a methylene group adjacent to a carbonyl occurs preferentially over that of a methyl group in a similar structural position. This difference



is particularly apparent in the case of 2-butanone where the product is acetic acid without any formation of propionic acid. For acetone a similar oxidation pathway will lead to the formation of acetic and formic acids. Since the latter is not stable to the reaction conditions used, its formation is surmised rather than verified. One possible explanation for the greater inertness of acetone to oxidation is that the reaction occurs with the enol form.⁸ We have verified that the small ratio of enol:keto form in acetone is not a likely explanation since acetophenone, which has an enol:keto ratio similar to 2-butanone and 3-pentanone, resembles acetone in being inert to oxidation.

The compounds $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Pt}(\text{PPh}_3)_3$ appear to be somewhat more effective than $\text{Rh}_6(\text{CO})_{16}$ for ketone oxidation. For these compounds the oxidation is carried out in the absence of carbon monoxide and the complex undergoes considerable decomposition with carbon dioxide being formed as a by-product. The solution nevertheless remains homogeneous and there is no formation of metal or metal oxide. For $\text{Rh}_6(\text{CO})_{16}$ the complex becomes soluble during the reaction. To verify homogeneity of reaction we have used the filtered solution as oxidation catalyst, and shown that the resulting liquid yields $\text{Rh}_6(\text{CO})_{16}$ under high pressures of carbon monoxide. The cluster compound was identified by comparison of the infrared spectrum in the carbonyl region with a synthetic sample and with literature values for $\nu_{\text{C}=\text{O}}$.⁹ Melting point and solubility data are also in agreement with reported data.¹⁰ The reactions show all the anticipated mechanistic features expected of a free-radical autoxidation process, and the failure to recover the complexes $\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{O}_2$ and $\text{Pt}(\text{PPh}_3)_2\text{O}_2$ from the reaction mixture is doubtless due to a concomitant oxidation of the coordinated carbonyl to carbon dioxide, and of the triphenylphosphine group to triphenylphosphine oxide. In a catalytic run using a large amount of the compound $\text{Pt}(\text{PPh}_3)_3$ we have isolated the ligand as triphenylphosphine oxide, which has been characterized by its melting point and infrared spectrum. We envisage a situation existing when $\text{Rh}_6(\text{CO})_{16}$ is used as catalyst where a series of mixed carboxylato carbonyl rhodium complexes exist in the solution. The initial concentration of carboxylic acid in the solvent is very low¹¹ but as the oxidation reaction proceeds the concentration of carboxylic acid increases, with a concomitant decrease in the pressure of carbon monoxide. Since it has been

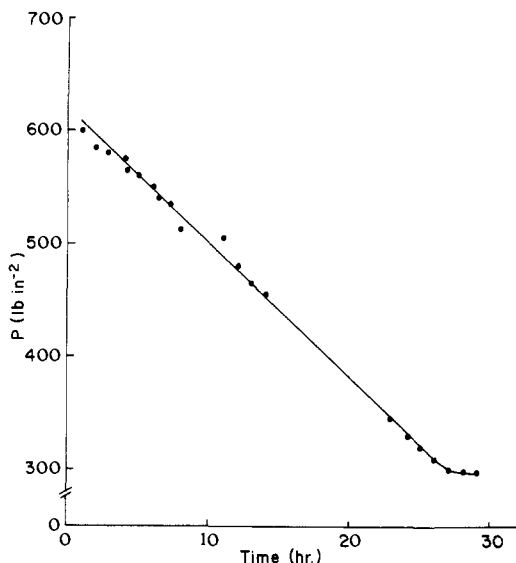


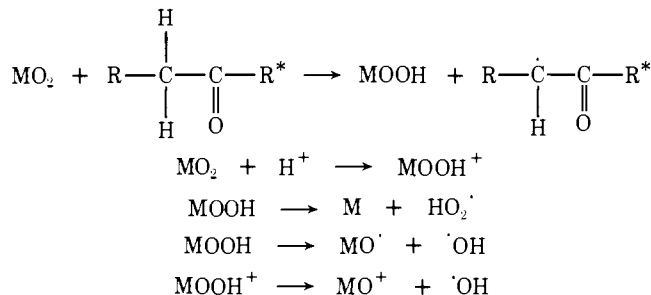
Figure 1. Rate plot for the oxidation of CO in acetone solution at $100 \pm 1^\circ\text{C}$. The initial pressures of CO and O_2 are 330 and 170 psi at 20°C . The solution contains $\text{Rh}_6(\text{CO})_{16}$ (15 mg) in acetone (10 mL).

previously reported that refluxing the compound $\text{Rh}_6(\text{CO})_{16}$ with carboxylic acid converts it into the carboxylato bridged dimer $[\text{Rh}(\text{OCOR})(\text{CO})_2]_2$,¹² such a compound must result at the end of the reaction when all the carbon monoxide has been oxidized. If the reaction vessel containing the catalyst solution is further pressurized with carbon monoxide and oxygen the reaction proceeds further. In a separate experiment we have confirmed that a synthetic sample of $[\text{Rh}(\text{OCOMe})(\text{CO})_2]_2$ is converted to $\text{Rh}_6(\text{CO})_{16}$ when placed under the pressure and solvent conditions of the oxidation reaction. We must assume therefore that the hexametallal cluster compound does not maintain its integrity throughout the reaction. It also appears unlikely to us that conversion of $\text{Rh}_6(\text{CO})_{16}$ to the carboxylato bridged dimer compound occurs by a single step reaction, and hence it is likely that other rhodium cluster aggregates are in significant amounts at different ratios of carbon monoxide:carboxylic acid concentration.

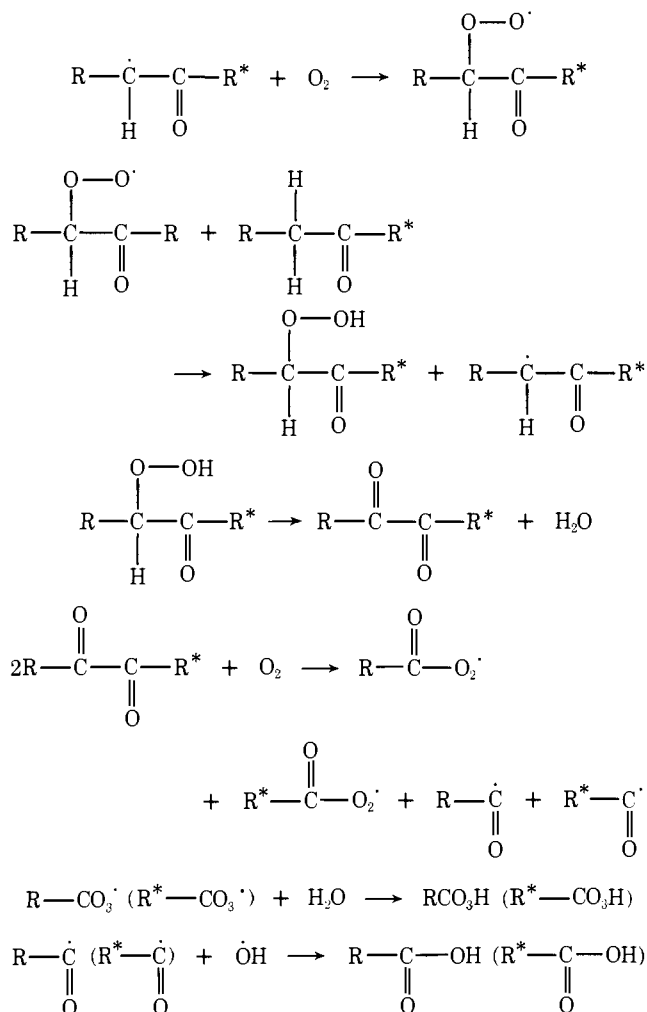
A number of experiments have been performed which verify that the oxidation proceeds via a free-radical pathway, making it similar to other platinum metal catalyzed autoxidations.⁴ Such a result is not unexpected by us but is particularly pertinent in view of the conclusions of Yuasa,³ who claims that the oxidation of benzaldehyde with the complexes $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Pt}(\text{PPh}_3)_3$ is a molecular process not involving free radicals. We find this to be a very surprising conclusion by these authors, especially in view of the greater facility for aldehydes to undergo free-radical autoxidation than ketones. The following reasons lead us to conclude that our oxidation reaction of ketones proceeds by a free-radical autoxidation mechanism. Firstly we find that the reaction, after initiation, proceeds at a rate which is linearly dependent with time, and is independent of oxygen pressure (Figure 1). We have also found that the oxidation reaction is inhibited by α -naphthol. When $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (37 mg) is present with 3-pentanone (10 mL) for 22 h at 80°C under an initial oxygen pressure of 500 psi, the quantity of acid produced is 30 mmol. When an identical experiment is performed with $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (32 mg) and α -naphthol (337 mg) for 49 h the yield of acid is only 2.6 mmol, thereby showing a considerable inhibition of the reaction by the presence of a free-radical scavenger. *As a caution* it should be noted that an explosion occurs on attempted oxidation of phenylacetone. We believe that this condition results from the buildup of too high concentration of the resonance stabilized benzyl radical. This situation results

in an explosive chain reaction as the temperature of the reaction is raised to 80°C , the minimum temperature for the oxidation reaction to occur. From these considerations we propose that the following initiation and propagation steps are involved in the reaction.¹³

Initiation:



Propagation:



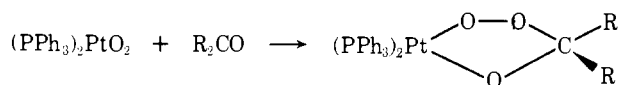
Transition metal hydroperoxide complexes of platinum metals are known and have been identified by earlier workers using EPR spectroscopy.¹⁴ In our catalytic oxidation of ketones such compounds can be readily formed by protonation of the transition metal oxygen complex from traces of carboxylic acid in the reagent ketone, or by abstraction of a labile hydrogen atom from the α -methylene group on the ketone. Following formation of such a hydroperoxide intermediate, homolytic fission of an oxygen-oxygen or metal-oxygen bond can readily occur to give hydroxyl or hydroperoxyl radicals. The propagation steps show how carboxylic acids RCO_2H and $\text{R}^*\text{CO}_2\text{H}$ can be formed in the autoxidation of ketone RCH_2COR^* . In

Table I

Ketone (10 mL)	Time, h	Temp, °C	Compd (μmol)	Pressure (psi)	Carboxylic acid, mequiv
Acetone	20	100	None	CO (330)/O ₂ (170)	<0.1
Acetone	29	100	Rh ₆ (CO) ₁₆ (41)	CO (330)/O ₂ (170)	0.8
2-Butanone	48	77	None	O ₂ (500)	0.5
2-Butanone	22	77	IrCl(CO)(PPh ₃) ₂ (47)	O ₂ (500)	11.0
3-Pentanone	19	80	None	O ₂ (500)	0.5
3-Pentanone	22	80	IrCl(CO)(PPh ₃) ₂ (48)	O ₂ (500)	30
3-Pentanone	49	80	IrCl(CO)(PPh ₃) ₂ (40)	O ₂ (500)	2.6
			α-Naphthol (2340)		
Cyclohexanone	19	80	None	O ₂ (500)	0.6
Cyclohexanone	21	80	IrCl(CO)(PPh ₃) ₂ (49)	O ₂ (500)	16.3
Cyclohexanone	22.5	77	Pt[O ₃ C(Me) ₂](PPh ₃) ₂ (40)	O ₂ (500)	3.0
Acetophenone	26	100	None	O ₂ (500)	0.1
Acetophenone	24	100	IrCl(CO)(PPh ₃) ₂ (38)	O ₂ (500)	0.1
Phenylacetone	<1	100	IrCl(CO)(PPh ₃) ₂ (41)	O ₂ (500)	Trace (explosion)

this reaction scheme we suggest intermediacy of a diketone, and it is pertinent to mention that we have found that under the reaction conditions prevailing 2,3-butanedione is oxidized to carboxylic acid faster than are monoketones. This contrasts with the oxidation of 2-butanone by ferric complexes of 1,10-phenanthroline where the *final product* is 2,3-butanedione.¹⁵ The peracid formed in the propagation steps can be readily converted to the carboxylic acid. The oxidation of ketones in the absence of a transition metal complex has been reported to occur at 140 °C to give carboxylic acids. In addition to using significantly higher temperatures, these workers initiated the reaction by addition of 1% of di-*tert*-butyl peroxide.^{16,17} We have made blank runs in the absence of metal complex to eliminate the possibility that initiation occurs equally effectively by homolysis in the absence of the transition metal compounds. The results show that the yield of carboxylic acid is considerably reduced (Table I). Our suggestion that the metal complex is involved in the initiation step does indeed appear to be valid, although concurrent with the oxidation of ketone the ligands on the complex itself suffer autoxidation. In this respect it is not strictly valid to refer to these complexes as catalysts since only for the case of Rh₆(CO)₁₆ is the compound amenable to recovery. For this latter compound the term catalyst is valid, but with no implication that the cluster structure is mechanistically significant in the reaction. Indeed upon initiation of the oxidation reaction the concomitant free-radical oxidation of carbon monoxide to carbon dioxide, and triphenylphosphine to triphenylphosphine oxide with the platinum and iridium compounds, will also be a source of free radicals for the ketone oxidation.

When Pt(PPh₃)₂O₂ is dissolved in ketone an addition reaction occurs and the species in solution is a cyclic ozonide complex Pt(O₃CR₂)(PPh₃)₂.^{18,19} Yuasa in his article on



benzaldehyde oxidation suggests that this adduct may somehow be involved as an intermediate in the oxidation reaction. Since these adducts are quite stable to the reverse reaction we considered it to be a possibility that the formation of such an acetone compound may be responsible for the failure of these triphenylphosphine compounds to oxidize acetone, especially since the peroxide-type bond in the complex shows no reactivity comparable to other peroxides. We have shown that the high stability of such complexes cannot be causing significant retardation to oxidation of a methyl group since the complex Pt(O₃CMe₂)(PPh₃)₂ from acetone is a very effective catalyst for the oxidation of cyclohexanone, thereby reinforcing our suggestion that the failure to observe acetone oxidation is a consequence of the greater difficulty in forming primary

radicals from methyl groups. The observed oxidation of acetone with Rh₆(CO)₁₆ may be a consequence of the concomitant oxidation of a considerable quantity of carbon monoxide where long free-radical chains are produced.

This carbon monoxide oxidation is an interesting side reaction. Our initial interest stems from our observation that the compound [Rh(PN)₂]PF₆ will both form a stable oxygen adduct and reversibly coordinate carbon monoxide.²⁰ On the supposition that the coordinated oxygen may be sufficiently activated for oxidation of CO we achieved the oxidation of CO to CO₂ in the presence of this compound. The formation of carbon dioxide was accompanied by the formation of Rh₆(CO)₁₆ and the oxide of *o*-(diphenylphosphino)-*N,N*-dimethylaniline (PN). The latter was isolated and compared with a synthetic sample. We must therefore conclude from the experiment that there is no positive evidence to suppose that [Rh(PN)₂]PF₆ is involved in the oxidation of CO to CO₂. We have not determined the ultimate catalyst turnover number for CO oxidation catalyzed by Rh₆(CO)₁₆, but it is noteworthy that after a mole ratio of 12 000:1 of CO:Rh₆(CO)₁₆ has been exceeded the catalytic activity of the solution is not significantly decreased. The complexes Pt(PPh₃)₃ and IrCl(CO)(PPh₃)₂ are not effective catalysts for the oxidation of CO to CO₂ at 100 °C under the same conditions of pressure as used with Rh₆(CO)₁₆.

When the oxidation of cyclohexanone is carried out in the presence of methanol or ethanol the final product is dimethyl or diethyl adipate. These compounds are formed in the esterification of the adipic acid produced and alcohol oxidation does not seem to be significant. Identification of the esters was made by gas chromatography, mass spectroscopy, and elemental analysis. By mass spectroscopy parent ions were not observed, the highest *m/e* value corresponding to an ion formed by loss of a single alkoxy group.

Our suggested mechanism involving a hydroperoxide intermediate leading to hydroxyl or hydroperoxyl radicals implies that the reaction should occur with any transition metal oxygen complex which can protonate on the coordinated oxygen. Of particular interest are the cobalt(II) complexes having an end-on bonded oxygen molecule, where a high electron density resides on the uncoordinated oxygen atom. This approach is particularly valid because of the recent report of the autoxidation of aldehydes by tetraphenylporphyrin cobalt(II) complexes.²¹ We have prepared the complex bis(salicylaldiminato)cobalt(II), and find that using 47 μmol of the complex in a mixture of 3-pentanone (5 mL) and pyridine (1 mL) for 24 h at 100 °C yields 6.6 mequiv of carboxylic acid. Using identical conditions in the absence of complex gives 7 × 10⁻³ mequiv of acid. We have also used the complex [Co(NH₃)₅O₂Co(NH₃)₅](NO₃)₄ (18 μmol) in the reaction under identical conditions except for the absence of pyridine,

and obtain a yield of 5.5 mequiv of carboxylic acid. With both complexes ligand oxidation occurs and the reaction mixture does not remain homogeneous.

Experimental Section

Complexes $\text{Rh}_6(\text{CO})_{16}$, $\text{Pt}(\text{PPh}_3)_3$, and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Co}(\text{salen})_2\text{O}_2$ were prepared by published procedures. Catalytic experiments were carried out in a Parr Model 4702 pressure vessel of 45-mL volume fitted with a 3000-psi gauge and break seal.²² A glass liner insert was used for the solution and a clean Teflon stir bar was used in the liner. Heating was carried out by a thermostated oil bath. Ketones were commercial samples and distilled prior to use. Carbon monoxide and oxygen were commercial samples free from carbon dioxide. Gas analyses were carried out on a Varian M66 mass spectrometer. Acids were characterized on a Varian gas chromatograph.

Quantitative Analysis of Carbon Dioxide and Carboxylic Acid. A vacuum line manifold system and 5-L three-necked flask, the latter containing a short length of rubber hose, was calibrated. To one arm of the flask was attached an evacuated gas analysis tube, and a known quantity of argon was admitted to the flask. The contents of the high-pressure reaction vessel were vented into the flask which was shaken to ensure complete mixing of all gaseous products. After mixing, a sample was admitted to the gas analysis tube which was assayed using the mass spectrometer. The data gave a peak height ratio for CO_2 (m/e 44) against Ar (m/e 40). After correcting for CO_2 peaks of lower m/e , a calibration plot was made of \log (pressure ratio of CO_2 :Ar) against \log (peak height ratio found from the electrometer). The pressure ratio of CO_2 :Ar was varied and measured using the calibrated flask and vacuum manifold. The order of introduction of the two gases did not affect the measured ratios. The plot showed a linear relationship and was used as a calibration chart for CO_2 .

Acetic and propionic acids were identified by gas chromatography using a 10% C-20 W column on 60/80 Chromosorb at 135 °C. Adipic acid was isolated for identification by extraction with 5% aqueous sodium bicarbonate solution followed by acidification and extraction with diethyl ether. Total acid equivalent was obtained by titration with a standardized sodium hydroxide solution.

Identification of Triphenylphosphine Oxide. To the contents of a catalytic reaction run using $\text{Pt}(\text{PPh}_3)_3$ (~500 mg) and 3-pentanone (15 mL) was added an aqueous solution of sodium hydroxide. The mixture was stirred and the base added until the solution had a pH greater than 9. The solution was extracted with ether and the ether layer separated. The ether was removed on a rotary evaporator, and the resulting triphenylphosphine oxide crystallized twice from benzene by addition of hexane, mp 154–157 °C, $\nu_{\text{P=O}}$ 1185 cm^{-1} .

***o*-(Diphenylphosphine oxide)-*N,N*-dimethylaniline.** To a mixture of *o*-(diphenylphosphino)-*N,N*-dimethylaniline (0.5 g) in ethanol (25 mL) at 50 °C was added hydrogen peroxide (1 mL of 30% solution).

The mixture becomes homogenous. The solution was heated at reflux for a few minutes and cooled to room temperature, and the volume of solution was slowly reduced to 0.5 mL on a rotary evaporator. To this solution was added water (5 mL) and the compound allowed to crystallize. The product was obtained as colorless needles: mp 132 °C; yield 0.26 g (50%); $\nu_{\text{P=O}}$ 1185 cm^{-1} ; τ_{Mc} 7.58. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{NOP}$: C, 74.8; H, 6.23; N, 4.36. Found: C, 75.2; H, 6.19; N, 4.45.

Acknowledgments. We wish to thank the National Science Foundation for support under Grant CHE 73-08793 A02. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Dr. T. B. Rauchfuss for preliminary experiments on the project.

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