

REACTIONS OF COORDINATED MOLECULES

I. THE OXIDATION OF TRANSITION METAL CARBENOID COMPLEXES BY IODOSOBENZENE; A COMPARATIVE STUDY

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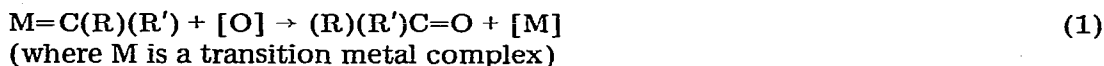
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Summary

The reaction of transition metal carbenoid complexes with oxidizing agents results in the oxidation of the carbenoid ligand forming the corresponding carboxylic acid derivative. A study of this reaction using pyridine-*N*-oxide, ceric ammonium nitrate and iodosobenzene as the oxidants reveals that the yield of the carboxylic acid derivative is affected significantly by the solvent medium. Oxidations using pyridine-*N*-oxide in tetrahydrofuran solution generally afford the organic acid derivative in good to excellent yields. Iodosobenzene is a selective oxidant affording the greatest yield of ethylene carbonate and it is the first oxidant reported to oxidize an amino-carbenoid complex to the corresponding amide. This oxidation reaction represents a convenient and rapid chemical method for the characterization of carbenoid complexes.

Introduction

Although the transition metal–carbenoid bond undergoes numerous chemical reactions [1,2], a reaction of particular importance is the oxidation of this bond which converts the carbenoid ligand into the corresponding organic carbonyl compound (eqn. 1). This reaction is useful since it provides chemical verification of a carbenoid ligand in an organometallic complex.



The oxidizing agents which have been used for this purpose are molecular oxygen, ceric ammonium nitrate and pyridine-*N*-oxide. Fischer and Riedmuller oxidized (alkoxy)(aryl)carbenoid complexes of the type $(OC)_5CrC(OCH_3)-(C_6H_4R)$ to the corresponding esters using molecular oxygen at 68°C [3]. Casey and Burkhardt mentioned a similar ester formation using ceric ammonium nitrate [4], and reported that the oxidation of the diphenyl-carbenoid complex, $(C_6H_5)_2-$

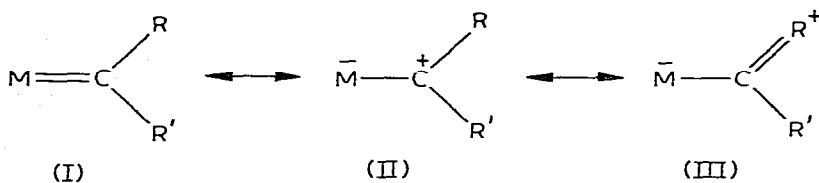
CW(CO)₅, by the same oxidant in ether solution at 25°C afforded benzophenone [5]. Cotton and Lukehart treated the complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{PPh}_3)(\text{CO})_2(\overline{\text{CCH}_2\text{-CH}_2\text{CH}_2\text{O})]\text{Br}$ with pyridine-*N*-oxide at 25°C and obtained γ -butyrolactone [6].

Since the oxidation of the carbenoid ligand to the carbonyl derivative would be a rapid and convenient chemical method for characterizing carbenoid complexes, we attempted to determine which oxidant produces the highest yield of the organic carbonyl product from the oxidation of a variety of carbenoid complexes at room temperature. Our search for a more versatile and conveniently handled oxidant revealed that iodosobenzene similarly oxidizes carbenoid complexes.

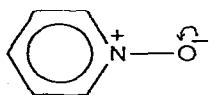
We report now a comparative study of such oxidations using pyridine-*N*-oxide, ceric ammonium nitrate and iodosobenzene as oxidizing agents. Six transition metal carbenoid complexes having metal atoms in both neutral and cationic oxidation states were oxidized forming five different types of organic carbonyl compounds. The oxidation reactions using pyridine-*N*-oxide in tetrahydrofuran solution give generally good to excellent yields of the organic carbonyl product, while iodosobenzene is a more selective oxidant. We feel that these oxidants can be used effectively and reliably for the characterization of transition metal carbenoid complexes.

Results and discussion

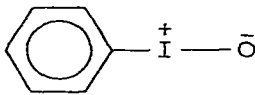
The electronic structure of the metal-carbenoid carbon bond is represented usually by three resonance forms (I-III) [1]. The addition of the carbenoid



ligand to highly polarized olefins occurs, presumably, through a four-center transition state having a considerable contribution from the 1,2-dipolar structure, II [7]. We felt that the oxidation of the metal-carbenoid-carbon bond by pyridine-*N*-oxide may proceed by a similar mechanism, since the polarity of the nitrogen-oxygen bond contributes significantly to the molecular dipole moment (IV) [8]. This possibility led us to examine iodosobenzene as an oxidizing agent



(IV)



(V)

for carbenoid complexes, since the iodine-oxygen bond in iodosobenzene is expected to be highly polarized, also (V) [9].

Oxidation reactions in methylene chloride solution

The results of the oxidation of the carbenoid ligands to the corresponding carboxylic acid derivatives in methylene chloride solution are shown in Table 1. Complexes VI-IX are neutral while the complexes X and XI are cationic. Compounds VIII and IX differ in the transition metal atom only. The organic acid derivatives are formed by the oxidative cleavage of the transition metal-carbenoid-carbon bond. The oxidation reactions which are reported in Table 1 were performed in methylene chloride solution under nitrogen at 25°C, and afforded ethylbenzoate, *N*-benzylacetamide, phenyl thioacetate, ethylene carbonate and γ -butyrolactone.

The tabulated yields are based on the amount of carbenoid complex used and are determined by standard GLC analysis. In all cases, the organic product was isolated by preparative gas-liquid chromatography and was identified by ¹H NMR and IR spectroscopy.

The oxidation reactions proceeded rapidly at 25°C with the concurrent evolution of a gas which is presumed to be carbon monoxide. Although gas evolution ceased after ten minutes, the reactions were continued for one hour. Longer reaction times did not increase the yield of the carboxylic acid derivative. The molar ratio of complex to oxidant was varied to optimize the yield of the organic carbonyl compound, and these values are enclosed within parentheses in Table 1.

The chromium and manganese complexes underwent oxidation affording green and dark brown precipitates, respectively. The infrared spectrum of these solids revealed only the presence of water and vibrations below 600 cm⁻¹ which were consistent with the spectra of the corresponding hydrated metal oxides, Cr₂O₃ · xH₂O and MnO₂ · xH₂O [10]. The water may have been absorbed from the atmosphere, since these solids were handled in air. A small amount of a brown solid precipitated during the oxidation of the tungsten complexes VI and IX. This solid turned blue when exposed to air and is assumed to be a tungsten-blue complex [11]. The only product containing molybdenum which was isolated from the oxidation of complex XI was (*h*⁵-C₅H₅)Mo(CO)₂(PPh₃)Br [12,13].

TABLE 1
THE OXIDATION OF CARBENOID COMPLEXES IN METHYLENE CHLORIDE SOLUTION AT 25°C

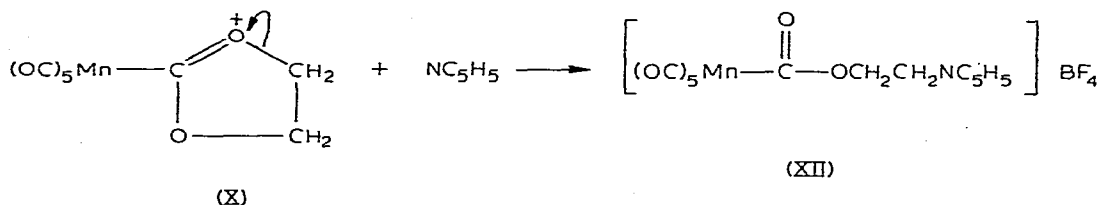
Complex	Carboxylic acid derivative	% Yield of carboxylic acid derivative for each oxidant ^{a, b}	
		Pyridine- <i>N</i> -oxide	Iodosobenzene
(OC) ₅ WC(Ph)(OEt) (VI)	PhC(O)OEt	57 (2/5)	36 (2/5)
(OC) ₃ CrC(Me)(NHCH ₂ Ph) (VII)	MeC(O)NHCH ₂ Ph	0	15 (2/5)
(OC) ₅ CrC(Me)(SPh) (VIII)	MeC(O)SPh	63 (2/5)	6 (2/5)
(OC) ₅ WC(Me)(SPh) (IX)	MeC(O)SPh	61 (2/5)	7 (2/5)
[(OC) ₅ MnCOCH ₂ CH ₂ O]BF ₄ (X)	C(O)OCH ₂ CH ₂ O	3 (1/3) ^c	21 (1/3) ^c
[CpMo(CO) ₂ (PPh ₃)COCH ₂ CH ₂ CH ₂]Br (XI)	C(O)OCH ₂ CH ₂ CH ₂	45 (1/1)	trace (1/1) ^c

^a Ratio in parentheses is the molar ratio of complex to oxidant which gave the maximum yield of the carboxylic acid derivative. ^b Yields based on complex assuming that one molecule of the carboxylic acid derivative could be formed per molecule of complex. ^c A competing reaction was detected.

The fate of the carbenoid ligand which is not oxidized to the carboxylic acid derivative is uncertain. Since carbenoid ligands undergo various intramolecular and intermolecular reactions [1,2], these other possible organic products are not of interest in establishing a general chemical method for the characterization of carbenoid complexes. However, those reactions marked by an asterisk in Table 1 indicate the observation of possible competing reactions. These reactions are discussed below.

Pyridine-*N*-oxide oxidized all of the carbenoid complexes forming the carboxylic acid derivative and pyridine except for the (methyl)(amino) carbenoid complex VII. In this instance no reaction occurred and complex VII was recovered unchanged. No other organic carbonyl products were formed during these oxidations, as determined by following the reaction by IR spectroscopy, except for the oxidation of complex X.

A pale yellow solid was isolated from this reaction and was identified as the pyridinium salt, XII. Presumably, this solid is formed by a pyridine-induced ring opening of the carbenoid ligand. The free pyridine is produced as a by-product



product from the oxidation of complex X. When complex X is treated with one equivalent of pyridine under identical conditions, complex XII is formed. The half-life of this ring opening reaction is 9.62 min at 25°C. This competing reaction accounts for the unusually low yield of ethylene carbonate. Similar ring opening reactions are known to occur for complex X [14], and this reaction is another example of the oxonium ion character exhibited by cationic carbenoid complexes, III [15,16]. Complex XI, however, does not undergo a ring opening when treated with pyridine under these conditions. Presumably, the oxonium ion character of complex X is increased significantly by the more electronegative Mn(CO)₅ group.

Iodosobenzene reacts with all six complexes forming the carboxylic acid derivative and iodobenzene. The relatively low yield of ethylene carbonate and the formation of only a trace amount of γ -butyrolactone is explained by the observation of a significant side-reaction. This reaction occurs only with complexes X and XI and is characterized by the appearance of a band at 1710 cm⁻¹. Preliminary results indicate that a unique oxidative ring opening reaction is occurring. These results will be reported later. The low yield of phenylthioacetate results presumably from the rapid oxidation of the metal atom rather than the metal-carbenoid bond. Iodosobenzene affords the highest yield of ethylene carbonate and it is the only oxidant which oxidizes the aminocarbenoid complex VII to the amide.

Oxidation reactions in tetrahydrofuran solution

Ceric ammonium nitrate does not react with the carbenoid complexes in

TABLE 2
THE OXIDATION OF CARBENOID COMPLEXES IN TETRAHYDROFURAN SOLUTION AT 25°C

Complex	Carboxylic acid derivative	% Yield of carboxylic acid derivative for each oxidant ^a		
		Pyridine- <i>N</i> -oxide ^b	Ceric Ammonium Nitrate ^c	Iodosobenzene ^b
VI	PhC(O)OEt	85	67	54
VII	MeC(O)NHCH ₂ Ph	0	0 ^d	13
VIII	MeC(O)SPh	73	31	trace
IX	MeC(O)SPh	77	14	3
X	C(O)OCH ₂ CH ₂ O	4 ^e	0 ^e	trace ^e
XI	C(O)OCH ₂ CH ₂ CH ₂	80	41	trace ^e

^a Yields based on complex assuming that one molecule of the carboxylic acid derivative could be formed per molecule of complex. ^b Same values for the molar ratio of complex to oxidant as shown in Table 1.

^c A 1/1 molar ratio of complex to oxidant gave the maximum yield of the organic carbonyl product.

^d Oxidant reacts rapidly with *N*-benzylacetamide at 25°C. ^e A competing reaction was detected.

methylene chloride solution due, apparently, to its very low solubility in that solvent. However, the carbenoid complexes are oxidized rapidly by ceric ammonium nitrate in tetrahydrofuran solution. The results of the oxidation of complexes VI-XI with all three oxidants in tetrahydrofuran solution at 25°C are shown in Table 2. The value of the molar ratio of complex to oxidant for the oxidation reactions using pyridine-*N*-oxide and iodosobenzene are the same as shown in Table 1. A 1/1 molar ratio of complex to ceric ammonium nitrate afforded the maximum yield of the carboxylic acid derivative.

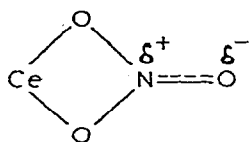
The oxidation reactions using pyridine-*N*-oxide in tetrahydrofuran solution afforded the organic carbonyl compounds in significantly higher yield than was found for this oxidant in methylene chloride solution. The only exceptions to this trend are complexes VII, which underwent no reaction, and X, where ethylene carbonate is formed in nearly the same yield. Complex X underwent the same pyridine-induced ring opening reaction as was observed in methylene chloride solution.

Conversely, the oxidation reactions using iodosobenzene in tetrahydrofuran solution gave generally lower yields of the carboxylic acid derivatives than was found for this oxidant in methylene chloride solution. Complex VIII was oxidized to only a slight extent and was recovered unchanged. Complexes X and XI underwent the same side-reaction as was observed in methylene chloride solution. No reaction between iodosobenzene and tetrahydrofuran was observed.

Ceric ammonium nitrate reacted with all six carbenoid complexes. However, the oxidation of complex VII did not afford even a trace amount of *N*-benzylacetamide. An independent study, treating all five carboxylic acid derivatives with each oxidizing agent in a 1/1 molar ratio, revealed that the only reaction which occurred was between ceric ammonium nitrate and *N*-benzylacetamide. This reaction was extremely rapid at 25°C with the amide disappearing completely within one minute of mixing the reactants. Complex X underwent a major side-reaction which was detected by the appearance of a sharp absorption at 1630 cm⁻¹ in the IR spectrum of the reaction solution. Although this product was not isolated, it may be an organic nitrate compound since ceric ammonium nitrate frequently produces such species during the oxidation of organic

molecules [17]. In general, pyridine-*N*-oxide afforded the highest yield of the carboxylic acid derivatives for the oxidation reactions conducted in tetrahydrofuran solution.

There is considerable uncertainty as to the source of the oxygen atom in the ceric ammonium nitrate oxidations reported here and by others [4,5]. Structure XIII suggests that one of the nitrato ligands may provide the oxygen atom,



(XIII)

since a bidentate nitrato ligand may be similar electronically to pyridine-*N*-oxide (IV) [18]. However, a more detailed investigation of both the reaction stoichiometry and the products of all of these oxidation reactions would be necessary in discerning the reaction mechanism.

Conclusion

The oxidation of transition metal carbenoid ligands to the corresponding carboxylic acid derivatives using pyridine-*N*-oxide, ceric ammonium nitrate and iodosobenzene is reported. The yield of the carboxylic acid derivatives resulting from oxidation of carbenoid complexes is sufficiently high using, selectively, either pyridine-*N*-oxide in tetrahydrofuran solution or iodosobenzene in methylene chloride solution that these oxidation conditions provide a convenient and versatile chemical method for the characterization of transition metal carbenoid complexes.

Experimental

All reactions were performed under dry, pre-purified nitrogen at 25°C. The following compounds were purchased: pyridine-*N*-oxide (Aldrich Chemical Co.), ceric ammonium nitrate (Matheson, Coleman and Bell), γ -butyrolactone, ethylbenzoate and ethylene carbonate. The compounds prepared by literature procedures are: iodosobenzene [19], $(OC)_5CrC(Ph)(OEt)$ [20], $(OC)_5CrC(Me)(NHCH_2Ph)$ [21], $(OC)_5CrC(Me)(SPh)$ [22], $(OC)_5WC(Me)(SPh)$ [22], $[(OC)_5MnCOCH_2CH_2O]BF_4$ [14], $[CpMo(CO)_2(PPh_3)CCH_2CH_2CH_2O]Br$ [6], *N*-benzylacetamide [23], and phenyl thioacetate [24].

The organic products were isolated from the reaction solution by preparative GLC using an Areograph Autoprep A-700 GLC having a 10 ft by 3/8 in glass column containing 10% 80/100 Chromabsorb Q. Organometallic products were isolated by normal column chromatographic procedures.

Infrared spectra were recorded on Perkin-Elmer 727 and 621 spectrometers. Solution spectra were obtained in 0.10 mm sodium chloride cavity cells using the solvent as a reference. Proton NMR spectra were obtained on a Jeol MH-100 NMR spectrometer.

Oxidation reactions and yield analysis

The general procedure used for the oxidation of the carbenoid complexes is as follows. Approximately 0.50 to 1.50 g of the carbenoid complex was dissolved in the organic solvent and treated with the oxidizing agent over a 1 min period in the molar ratios provided above. The methylene chloride was dried over MCB 4A molecular sieves and the tetrahydrofuran was distilled before use. Vigorous gas evolution occurred during the first 10 min of the reaction along with a fading in the initial color of the reaction solution. In all cases a small amount of precipitate was formed. The reaction solution was stirred for 1 h and then filtered and analyzed by GLC. All yields are based on the amount of carbenoid complex used and were determined by measuring the GLC peak area of the carboxylic acid derivative found in the reaction solution and in standard solutions.

Preparation of [(OC)₅MnC(O)OCH₂CH₂NC₅H₅]BF₄ (XII)

A solution of 0.14 g (0.40 mmol) of X in 4 ml of acetone was treated with 0.02 g (0.25 mmol) of pyridine at 25°C. The reaction solution was stirred for 1 h. XII [0.093 g (85% based on pyridine)], an off-white solid (dec 123-125°C), was crystallized from the reaction solution by adding ether until the solution became cloudy and then cooling to -20°C. IR: (CH₂Cl₂): ν(CO), 2130 w, 2030 vs (br), ν(acyl), 1620 m; ¹H NMR: (CD₃CN); τ 1.09 (d, 2, NC₅H₅), 1.25 (t, 1, NC₅H₅), 1.77 (t, 2, NC₅H₅), 5.14 (t, 2, CH₂) and 5.46 ppm (t, 2, CH₂). Since complex XII underwent noticeable thermal decomposition within 15 min at 25°C, it was dissolved in a minimum amount of acetonitrile and treated with one equivalent of LiBr. A strong smell of pyridine was detected. Removal of the solvent at reduced pressure and extraction of the residue with hexane afforded the known complex, (OC)₅MnC(O)OCH₂CH₂Br [14].

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