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TRIMETHYLAMINE *N*-OXIDE—A VERSATILE REAGENT FOR ORGANOMETALLIC CHEMISTRY

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CONTENTS

ABBREVIATIONS

bipy	2,2′-bipyridine
COD	cyclooctadiene
DMEO	*N*,*N*-dimethylethylenediamine *N*-oxide
dppe	bis(diphenyldiphosphino)ethane
NBD	norbornadiene
TENO	triethylamine *N*-oxide
TMNO	trimethylamine *N*-oxide
TPNO	tripropylamine *N*-oxide
tpy	2,2′,2″-terpyridine

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A. INTRODUCTION

The organic chemistry of amine *N*-oxides is rich [1–4]. Numerous examples illustrate that this type of compound can serve as an oxidant in organic and organometallic chemistry, and as a ligand in coordination chemistry. Several reviews of coordination complexes formed by transition metals with heteroaromatic amine *N*-oxides [5–9] and with trialkyl- and triarylphosphine and arsine oxides [9] have appeared. A brief account of the metal complexes of aliphatic amine *N*-oxides was mentioned in 1973 in one of several review articles on metal complexes of aromatic amine *N*-oxides [7]. Since then, several important contributions have been reported in the literature. Moreover, during the last decade, great interest in the use of trimethylamine *N*-oxide (TMNO) in organometallic chemistry has been shown by the significant number of publications in the literature. The present review is mainly concerned with the coordination and organometallic chemistry of TMNO. Particular emphasis will be placed on the use of TMNO in the decarbonylation reactions of metal carbonyl derivatives and in the liberation of organic ligands from the corresponding metal complexes. The chemistry of related aliphatic amine *N*-oxides will also be covered briefly.

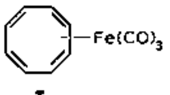
B. DECARBONYLATION REACTIONS

(i) Generalities

The first reaction of a metal carbonyl with an amine *N*-oxide was discovered in 1959 [10] when pyridine-*N*-oxide was treated with $Fe(CO)_5$ to give hexakis-(pyridine-*N*-oxide)–iron^{II}-tridecacarbonyltetraferrate. It was later found that aliphatic, aromatic and heterocyclic amine oxides were all readily deoxygenated by $Fe(CO)_5$ in boiling butyl ether to the corresponding amines [11]. Thus, brucine *N*-oxide hydrate was reduced to brucine [11]. It was noted that one mole of carbon dioxide was formed from each mole of pyridine-*N*-oxide deoxygenated [11]. It was not until 1975 that Shvo and Hazum first reported a facile synthesis in moderate to good yield of organic iron carbonyl complexes by using amine oxides to promote complexation of diene ligands with the metal carbonyl moiety [12].

The reaction conditions are very mild and complexation usually proceeds at room temperature or below. For example, cyclooctatetraenetricarbonyliron **I** was prepared in excellent yield by this method [12]. Similarly, **II** was obtained in 62% yield [12]. Various solvents, from non-polar, e.g. benzene, to polar aprotic, e.g. acetone, can be used.

The key step in this reaction is to oxidize the CO ligand so that an unsaturated organometallic moiety can be generated to accommodate the



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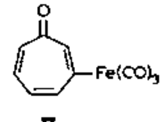
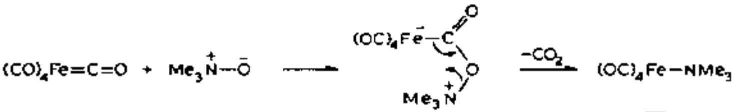


II

diene ligands. Some studies on the reaction mechanisms have been reported. On treatment with a two-fold excess of TMNO at $-30\,°C$, $Fe(CO)_5$ was smoothly transformed into aminotetracarbonyliron **III** [13–16]. In a similar manner $(CO)_5MNMe_3$ (M = Cr, Mo or W) [17] and *cis*-$PhMn(NMe_3)(CO)_4$ [18] were obtained. The mechanism for this transformation is shown in eqn. (1) [13]. The complex **III** has been suggested as the intermediate for the preparation of diene–tricarbonyliron complexes from diene, TMNO and $Fe(CO)_5$ [13]. This argument is based on the reaction of **III** with cyclooctatetraene to give the corresponding tricarbonyliron complex **I** in 55% yield [13]. On the other hand, many examples indicate that **III** behaves similarly to $Fe_2(CO)_9$, which has been proposed to generate the unsaturated species $Fe(CO)_4$ as an intermediate [19]. Accordingly, $Fe(CO)_4$ was suggested as the intermediate (eqn. 2) [11]. A reversible dissociation of **III** has been proposed (eqn. 3) [16]. It is noteworthy that the amine complexes, such as **III**, decompose at room temperature and the rate of the isomerization of 1-heptene with **III** or related amine complexes is somewhat slower than that with $Fe_2(CO)_9$, but is faster than the isomerization with $Fe(CO)_5$ [16]. Furthermore, a different product distribution was found in the reaction of 2-phenylmethylenecyclopropane with $Fe(CO)_5$ and TMNO and with $Fe_2(CO)_9$ (eqn. 4) [20,21].



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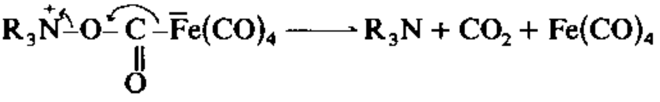
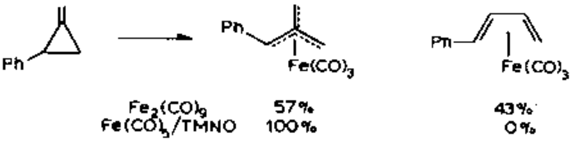
III



$$R_3\overset{+}{N}-O-\underset{\underset{O}{\|}}{C}-\bar{F}e(CO)_4 \longrightarrow R_3N + CO_2 + Fe(CO)_4 \qquad (2)$$

$$R_3NFe(CO)_4 \rightleftharpoons R_3N + Fe(CO)_4 \qquad (3)$$



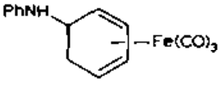
(4)

Not all carbonyl ligands can be attacked by TMNO. Empirical studies indicate that there is a reasonable correlation between the reactivity of the metal carbonyl and TMNO, and stretching force constants based on a simple energy-factor force [18,22]. A parallel between $\nu(CO)$ and the severity of the reaction conditions in metal carbonyl–amine oxide reactions has been suggested; similar correlations exist for nucleophiles such as amines [23] and organolithium compounds [24]. Consequently, Koelle [17] and Brown and coworkers [18] concluded that the requirements that $K > 16.0$ and/or $\nu(CO) > 2000$ cm^{-1} are useful guidelines for predicting whether an amine oxide reagent will react with a given substrate.

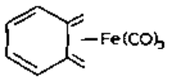
(ii) Intermolecular ligand displacement reactions

(a) Mononuclear metal carbonyl and its derivatives

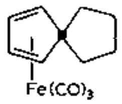
Certain complexes which cannot be prepared readily by other means can be synthesized by direct complexation in the presence of TMNO. To illustrate, $Fe(CO)_5$, 5-anilinocyclohexa-1,3-diene and TMNO in benzene gave the corresponding diene complex **IV** [12] which can otherwise be obtained indirectly [28]. The *o*-xylylenetricarbonyliron complex **V** was prepared similarly [12]. Spirononadienetricarbonyliron **VI** was synthesized in good yield [29]. It is interesting to note that **VI** is quite stable and that the organic ligand remains intact (cf. Section C) in refluxing benzene in the presence of TMNO and $Fe(CO)_5$, whereas rearrangement of **VI** occurs on treatment with $Fe_2(CO)_9$ under similar conditions [29]. Several $Fe(CO)_3$–diene complexes with various functional groups were prepared [30,31]. NBD–$W(CO)_4$ was synthesized from $W(CO)_6$, NBD and TMNO [17].



IV



V



VI

The preparation of isonitrile complexes, $Fe(CO)_{5-n}(CNR)_n$ ($n = 1, 2$), was found to be catalysed by TMNO [25,26]. Several triphenylphosphine [17,32], carbon disulphide [32], acetonitrile [17], and amine complexes [13,14,17] were synthesized by this method.

The trimethylamine complex **III** thus obtained has been shown to be very useful in promoting homolytic cleavage of the carbon–halogen bond under moderate conditions [13,14], whereas elevated temperatures are generally required when the parent pentacarbonyliron is employed [34–36]. The chromium analogue, $Me_3NCr(CO)_5$ [17] has been found to react with $[(\eta^6\text{-}C_6H_5)As(C_6H_5)_2]Cr(CO)_3$ to give $(OC)_3Cr[(\eta^6\text{-}C_6H_5)(C_6H_5)_2As]Cr(CO)_5$

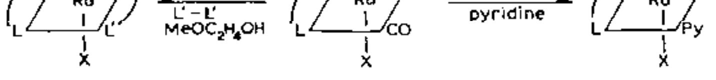
[27]. The alkyl ligand was found to remain intact in the ligand substitution reaction promoted by TMNO [33].

Several metal carbonyl derivatives of a water-soluble phosphine were explored [37,38]. Their syntheses involve the reaction of the appropriate phosphine ligand, TMNO and respective metal carbonyls.

Substitution reactions of $PhMn(CO)_5$ with phosphines and arsines proceeded rapidly at room temperature in the presence of TMNO to give *cis*-$PhMn(CO)_4L$ [18]. In a similar manner, $(\eta^5\text{-}C_5H_5)M(CO)_3X$ ($M = Mo$ or W; X = halide) gave *cis*-$(\eta^5\text{-}C_5H_5)M(CO)_2LX$ [18]. It is noteworthy that stereoselectivity, product yields and reaction rates are dramatically enhanced by the use of the amine oxide reagent [18].

Replacement of CO ligands by other phosphine or phosphite ligands in cationic organotransition metal complexes can also proceed efficiently. The two CO ligands in the cation, $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$, were replaced by phosphine ligands ($L = Ph_3P$, $Ph_2(CH_2)_nPPh_2$, $n = 1, 2, 3$) or trimethylphosphite in quantitative yield upon treatment with excess TMNO [39]. Alkaline hydrogen peroxide can also be used to catalyse these reactions. It is noteworthy that the usual complications arising from Michaelis–Arbuzov-type rearrangements of phosphite complexes to phosphonate complexes [40] can be avoided. The CO ligand in $[(\eta^5\text{-}C_5H_5Re(NO)(CO)L]^+$ was substituted by a phosphine ligand in the presence of TMNO [41]. Replacement of CO with anionic species was promoted by TMNO [42].

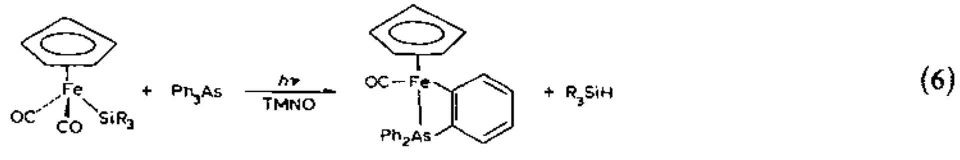
Selective replacement of one CO ligand of $Ru(CO)_2X_2L_2$ complexes ($X = Br$ or CF_3CO_2; L_2 = phen, bipy or Ph_3P) was achieved by the reaction with TMNO in pyridine (eqn. 5) [43]. It is interesting to note that the $\nu(CO)$ in the product is found in the region of 1940 cm^{-1} [43]. This carbonyl group cannot be removed, even in boiling pyridine, which seems to be consistent with the observation that TMNO-induced decarbonylations are generally restricted to carbonyls with $\nu(CO) > 2000$ cm^{-1} [18]. However, a recent report showed that this barrier can be overcome by choosing 2-methoxyethanol as solvent [44]. Thus, both carbonyl groups were removed on reaction with bidentate ligands and TMNO (eqn. 5) in boiling 2-methoxyethanol, even though the reaction proceeds through an intermediate monocarbonyl with $\nu(CO) < 2000$ cm^{-1} [44]. It is noteworthy that no decarbonylation was achieved in the absence of amine oxide. Furthermore, complexes such as $[RuCl(bipy)(tpy)]PF_6$ and $[Ru(L_2)_3](PF_6)_2$ were prepared from $Ru(CO)_2Cl_2L_3$ [44]. This study suggested that TMNO-induced de-



(5)

carbonylations can be achieved with $\nu(CO) < 2000\ cm^{-1}$.

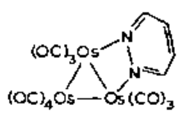
Photochemically induced cyclometallation has been found to be accelerated by TMNO (eqn. 6) [45].



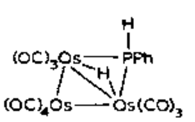
(b) Multinuclear metal carbonyl derivatives

TMNO is particularly useful in the decarbonylation reactions of multinuclear metal carbonyl derivatives. Conventional thermo- or photo-induced ligand displacement procedures are complicated by the cleavage of the metal–metal bond which leads to a complexity of products. To illustrate this, photo-catalysed substitution of a CO ligand in $Mn_2(CO)_{10}$ by pyridine resulted in the monosubstituted product in only 3–7% yield [46], whereas in the presence of TMNO, an excellent yield was obtained [47]. Similarly, $Re_2(CO)_9L$ ($L = RNH_2$, pyridine, MeCN) and $Re_2(CO)_8L_2$ were prepared [47,162].

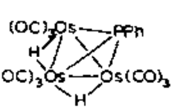
$(MeCN)Os_3(CO)_{11}$ and $(MeCN)_2Os_3(CO)_{10}$ have been shown to be very useful starting materials for synthesizing various substituted osmium clusters [48–52]. These acetonitrile complexes were readily prepared from $Os_3(CO)_{12}$ and TMNO in acetonitrile [48–51]. In addition, (1,2-diazine)decacarbonyl-triangulo-triosmium **VII** was synthesized from a slurry of $Os_3(CO)_{12}$ and pyrazine in the presence of TMNO in 86% yield [53]. $Os_3(CO)_{12}$ reacted with phenylphosphine in the presence of TMNO to give **VIII** and **IX** [54]. Treatment of $Os_3(CO)_{12}$ with TMNO in acetonitrile followed by excess $HRe(CO)_5$ afforded $HReOs_3(CO)_{16}$ [50]. Furthermore, $Os_3(CO)_{10}(MeCN)_2$ treated with $HRe(CO)_5$ in the presence of one equivalent of TMNO in acetonitrile gave $HReOs_3(CO)_{15}$, whereas treatment of $Os_3(CO)_{10}(C_8H_{14})_2$



VII



VIII

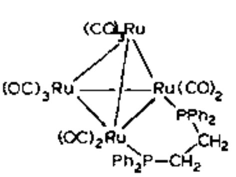


IX

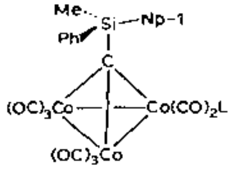
with excess $HRe(CO)_5$ resulted in a different product, $H_2Re_2Os_3(CO)_{20}$ [50]. $H_2Re_2Os_3(CO)_{20}$ and $HReOs_3(CO)_{16}$ readily underwent a decarbonylation reaction on treatment with TMNO to give $H_2Re_2Os_3(CO)_{19}$ and $HReOs_3(CO)_{15}$, respectively [50].

The reaction of the ruthenium cluster, $(\mu\text{-}H)_4Ru_4(CO)_{12}$ with dppe and

TMNO yielded the phosphine-substituted product **X** [55]. $Ir_4(CO)_{12}$ was refluxed with COD and TMNO in THF to give a mixture of two products, which further reacted with excess COD at elevated temperatures in the presence of TMNO to give $Ir_4(CO)_6(COD)_3$ [56]. The cobalt cluster **XIa** also underwent a ligand replacement reaction in the presence of TMNO to give **XIb** [57]. It is noteworthy that no further substitution reaction was observed in **XIb**.



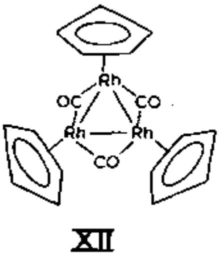
X



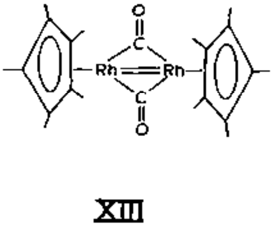
XI a L = CO
b L = $PhMe_2P$

(iii) Oligomerization of mononuclear metal carbonyl derivatives

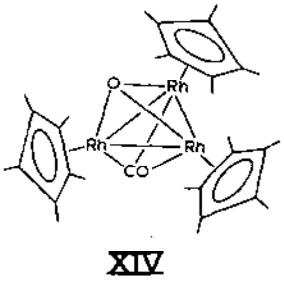
As mentioned above, unsaturated intermediates are conveniently generated by the oxidative decarbonylation reaction. In the absence of other ligands, these unsaturated species can undergo oligomerization reactions. Thus, the interaction of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with anhydrous TMNO provided an efficient route to **XII**, together with a dimer $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$



XII



XIII

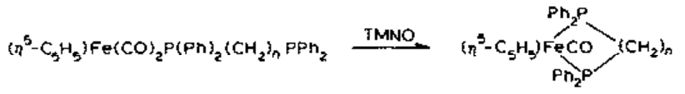


XIV

and a tetramer $(\eta^5\text{-}C_5H_5)_4Rh_4(CO)_2$ [58,59]. On the other hand, treatment of $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ with TMNO hydrate gave, in addition to the desired dimer **XIII**, a trinuclear μ_3-oxo-complex **XIV** in 10% yield [60]. The mechanism for the formation of the latter compound is not clear. The reaction between $(\eta^5\text{-}C_5H_5)Co(CO)_2$ and $Me_3SiC_2SiMe_3$ in the presence of TMNO as decarbonylation reagent gave $(\eta^5\text{-}C_5H_5)_2Co_2(CO)(Me_3SiC_2SiMe_3)$ in 78% yield [61]. On the other hand, the corresponding rhodium analogue produced a number of unidentified products [61].

(iv) Intramolecular ligand displacement reactions

Several reports concerning TMNO-promoted intramolecular ligand displacement reactions have appeared. Thus, the second phosphine moiety of a bidentate ligand has been found to replace a carbon monoxide ligand in essentially quantitative yield on using TMNO as oxidant (eqn. 7) [39].

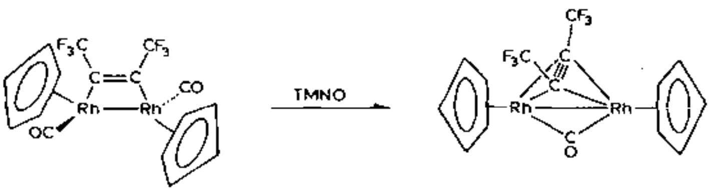


$$(\eta^5\text{-}C_5H_5)Fe(CO)_2P(Ph)_2(CH_2)_nPPh_2 \xrightarrow{TMNO} (\eta^5\text{-}C_5H_5)FeCO(Ph_2P)_2(CH_2)_n \qquad (7)$$

The TMNO-induced rearrangement of σ-allyl complexes to π-allyl complexes has been discovered recently (eqn. 8) [62]. The yields are very good. It is noted that the corresponding methyl analogue does not undergo a decarbonylation reaction under similar reaction conditions [18], although both complexes exhibit similar infrared absorptions in the carbonyl region. This method provides a convenient method of synthesizing π-allylmolybdenum complexes.

$$(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_2CH=CH_2) \overset{TMNO}{\rightarrow} (\eta^5\text{-}C_5H_5)Mo(CO)_2\rangle \qquad (8)$$

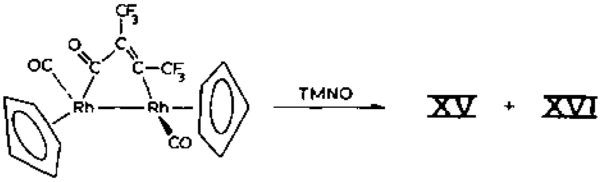
Treatment of *trans*-$(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2(\mu(\eta^2\text{-}CF_3C_2CF_3))$, **XV** [63] with TMNO gave a green complex **XVI** in 70% yield (eqn. 9) [64,65].



XV XVI (9)

(v) Deinsertion reactions

TMNO has also been found to induce deinsertion reactions. Thus, (η^5-$C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3CO)$ was allowed to react with TMNO to yield a mixture of deinsertion products (eqn. 10) [66].



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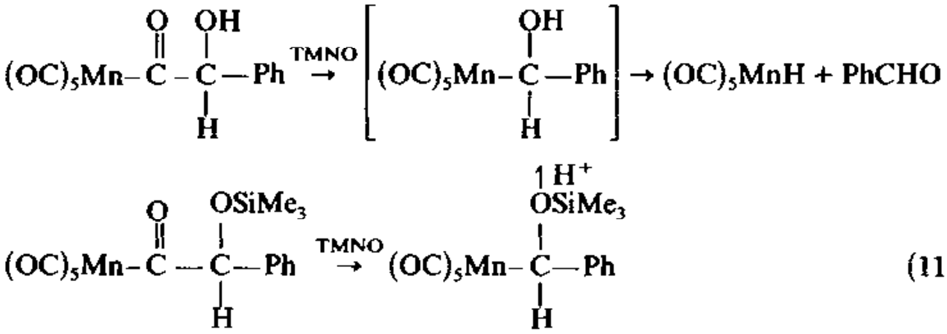
α-Siloxy and α-hydroxy manganese alkyls were obtained from the decarbonylation of the corresponding siloxy- and hydroxy-acyl complexes upon treatment with a stoichiometric amount of TMNO (eqn. 11) [67]. It is noted that photolysis has not proved to be a feasible method for this purpose [67].



$$(OC)_5Mn-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-Ph \xrightarrow{TMNO} \left[(OC)_5Mn-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-Ph\right] \rightarrow (OC)_5MnH + PhCHO$$

$$\uparrow H^+$$

$$(OC)_5Mn-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{OSiMe_3}{|}}{C}}-Ph \xrightarrow{TMNO} (OC)_5Mn-\underset{\underset{H}{|}}{\overset{\overset{OSiMe_3}{|}}{C}}-Ph \qquad (11)$$

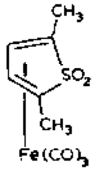
C. LIBERATION OF ORGANIC LIGANDS

(i) Generalities

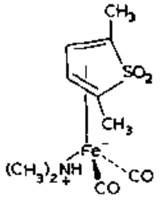
The use of organometallic compounds in organic synthesis may be one of the most important research areas in chemistry nowadays [68]. Organometallic compounds usually serve as templates which can control the regiochemistry and, in many cases, the stereochemistry of reactions. Various agents, such as Ce^{IV} [69], I_2 [70], and Fe^{III} [71] have been used to disengage the organic ligands. Although successful with structurally simple cases, the inherent disadvantage of these methods is the instability of the π-electron-rich organic ligands under the oxidative reaction conditions. Furthermore, easily oxidizable functional groups may not survive under these reaction conditions.

Shvo and Hazum were the first to use TMNO to induce the disengagement of organic ligands from $(CO)_nFeL$ complexes in good yield [72]. It is noted that no detectable deterioration of the product has been found under the reaction conditions. Aprotic solvents are generally used. In order to drive the reaction to completion, and at reasonable rates, a large excess of TMNO must be used.

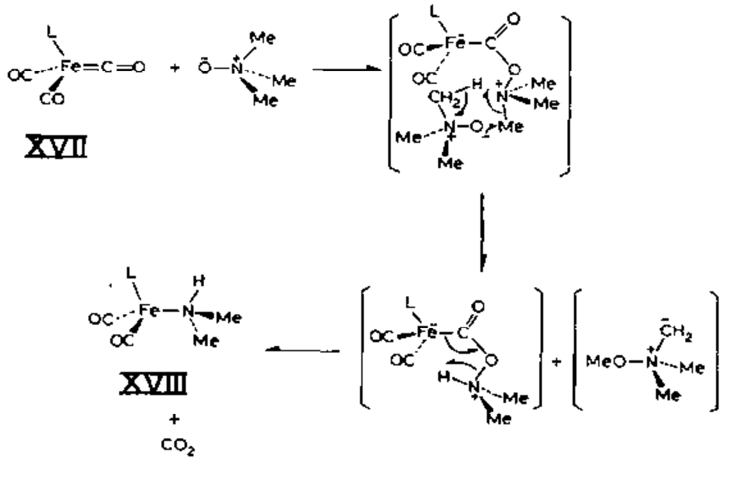
The mechanism of this reaction has not been explored fully. TMNO may serve as an oxidant to oxidize the metal so that the metal–ligand bond may be destabilized. Trimethylamine may be liberated during the course of the reaction [72]. On the other hand, the reaction of the 2,5-dimethylthiophene-*SS*-dioxide tricarbonyliron complex **XVII** with TMNO gave an intermediate compound **XVIII** containing a dimethylamine ligand [73], which can further react with TMNO to disengage the organic ligand. The proposed mechanism for this transformation is outlined in eqn. (12) [73]. It is noteworthy that the first step may also involve nucleophilic attack at the carbonyl group. It is known that transition metals can either be oxidized by amine oxide [74] or promote Pummerer-type reactions of amine oxide [75].



XVII



XVIII

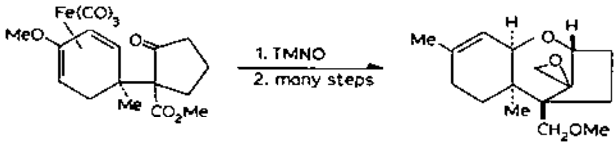


(12)

At the present stage, the reaction is mainly confined to the disengagement of ligands from the corresponding iron carbonyl complexes. Attempts to liberate organic ligands from organometallic compounds without carbonyl ligands were not successful [76,77]. The potential extension of this method to other metal complexes is yet to be explored.

(ii) η^4-Diene ligands

The use of organoiron in organic synthesis is well documented [78–80]. There are numerous examples in the literature of the addition of nucleophiles to a pentadienyl iron carbonyl cation, giving diene–ironcarbonyl complexes. Diene ligands thus obtained have been released successfully by means of TMNO [81–105]; various 5,5-disubstituted cyclohexadienes were synthesized in this way. This method has been employed in the total synthesis of natural products (eqns. 13–15) such as trichothecenes [89–94], steroids [95,96], alkaloids [97,99] and even macrolides [100]. A similar approach has been used to prepare cycloheptadienes [100,101] and *trans*-5,6-dihydroxycyclohexadiene [102].



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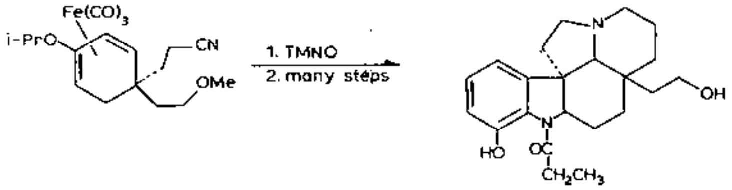
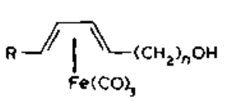


(14)

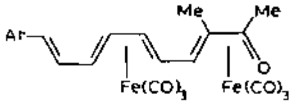
(15)

Insect pheromones were synthesized by disengagement of the organic ligands from the corresponding tricarbonyliron complexes **XIX** [107] and **XX** [108]. Metal complexes containing a vinyl borane function were also oxidized by TMNO (eqn. 16) [109].

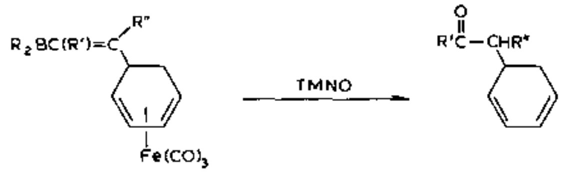
Oxidation-sensitive 5-anilino-1,3-cyclohexadiene was isolated in 45% yield by the reaction of the corresponding tricarbonyliron complex **IV** with



XIX



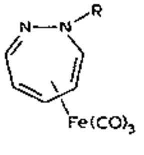
XX



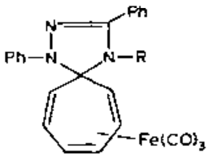
(16)

TMNO [72]. Several nitrogen-containing diene moieties were regenerated from their tricarbonyliron complexes upon treatment with TMNO [97–99,104–106]. Liberation of the heterocyclic ligand from **XXI** was reportedly in excellent yield [110]. On the other hand, the rearranged product **XXIII** or its isomer was obtained when the complex **XXII** was treated with TMNO [111]. The metal carbonyl fragment of (*N*-carbomethoxy-1,2-dihydropyridine)iron tricarbonyl **XXIV** was easily removed by reacting the complex with TMNO [112]. Decomplexation of the tricarbonyl-(germacyclopentadiene)iron complex **XXV** with TMNO took place smoothly [113].

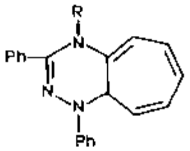
6-Isopropylidenecycloheptadienone was recovered without migration of the double bond when the corresponding complex **XXVI** was allowed to react with TMNO [114]. The cyclopropane moiety was found to be stable under the reaction conditions [115]. It is noted that the ligand in **XXVII** underwent rearrangement or oxidation when the complex was allowed to react with TMNO (eqn. 17) [116].



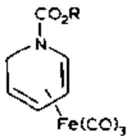
XXI



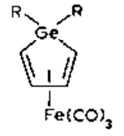
XXII



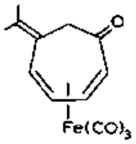
XXIII



XXIV

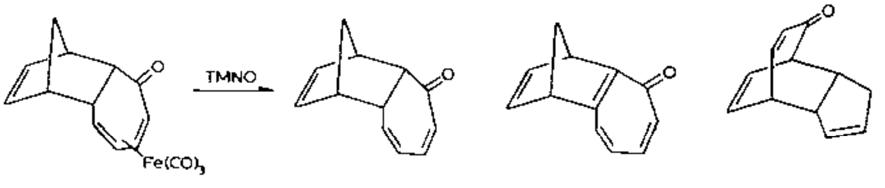


XXV



XXVI

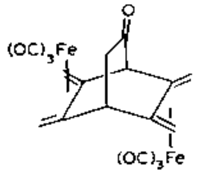
The tricarbonyliron moiety can also serve as a protective group for dienes in steroids [117] and strained ring compounds [118–123]. Thus, cyclobutadiene was liberated from its iron complex upon treatment with amine oxide [118,119]. Exocyclic dienes were regenerated from their metal com-

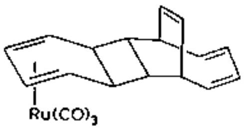


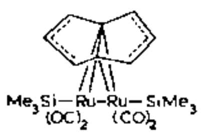
(17)

XXVII

plexes **XXVIII** [120–123]. The metal moieties of bis-metal complexes can be removed stepwise [122,123] or simultaneously [108,124].





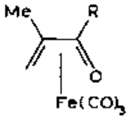


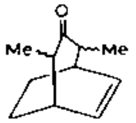
XXVIII **XXIX** **XXX**

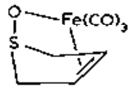
Cleavage of the ruthenium and π-diene linkage in **XXIX** is promoted by TMNO [125]. On the other hand, attempts to disengage the pentalene ligand from the diruthenium complex **XXX** resulted in a mixture of organic compounds [126].

(iii) Miscellaneous ligands

η^4-Complexes of enones **XXXI** [72,127,128] were treated with TMNO in order to liberate the organic moiety in good yield. Non-conjugated diene ligands such as norbornadiene can also be decomplexed smoothly from the corresponding tricarbonyliron complex [72]. The adduct from the Noyori reaction [129] was treated with TMNO to disengage the organic ligand **XXXII** [130]. Dihydrothiophene oxide was liberated from the corresponding tricarbonyliron complex **XXXIII** [131].

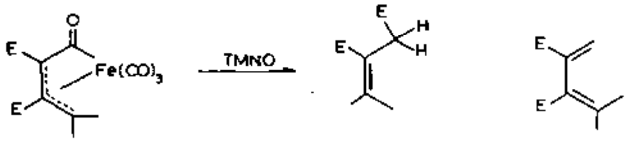






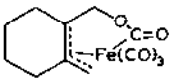
XXXI **XXXII** **XXXIII**

Several functionalized ($\eta^3:\eta^1$-allylcarbonyl)iron tricarbonyl complexes, obtained from electrophilic *gem*-dimethylcyclopropenes [132] were oxidized with TMNO in methanol (eqn. 18) [133]. This reaction provides a useful route for the synthesis of the valuable vinylketene synthon [133]. Similarly, the allyl complex **XXXIV** was treated with TMNO to give **XXXV** [134]. The barbaralyl system **XXXVI** was obtained from the reaction of the complex **XXXVII** with TMNO [135].

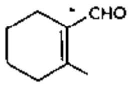


(18)

The trimethylenemethane intermediate, 2-methylenecyclopentane-1,3-diyl **XXVIII** was recently generated from the corresponding iron complex **XXXIX**

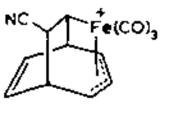


XXXIV



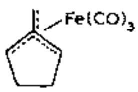
XXXV

XXXVI



XXXVII

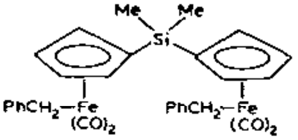
XXXVIII



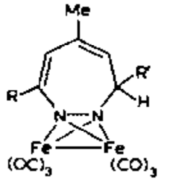
XXXIX

[136]. The intermediate was trapped with diethyl fumarate and the results were compared with related work [137,138].

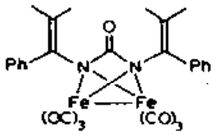
There is no direct evidence to suggest that cleavage of the metal–carbon bond is catalysed by TMNO. In fact, several σ-metal–carbon bonds such as those found in σ-arylmanganese [18] and methylmolybdenum [18] compounds are stable under the reaction conditions. Similar to the photochemical process, **XL** gave bibenzyl as the major organic product upon treatment



XL



XLI



XLII

with TMNO, which was reported to initiate the first decarbonylation step [139]. In addition, photo-induced liberation of trialkylsilane was accelerated in the presence of TMNO (eqn. 6) [45].

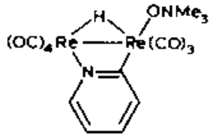
Various nitrogen ligands were also disengaged from the corresponding tricarbonyliron complexes, **XLI** and **XLII** [140,141].

D. STABLE METAL COMPLEXES

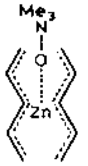
(i) Generalities

Unlike heteroaromatic amine-*N*-oxides [5–9], a relatively small number of metal complexes formed with TMNO and related aliphatic amine *N*-oxide ligands are known. As discussed in previous sections, aliphatic amine *N*-oxides behave as oxidants to oxidize the CO ligand, thus generating coordinatively unsaturated species and to oxidize the metal centre, thus liberating organic ligands. The aliphatic amine *N*-oxide complexes seem to be much more difficult to form and less stable than those of the heteroaromatic amine *N*-oxides. Thus, $Co(TENO)_4(ClO_4)_2$ decomposes to cobalt oxide and triethylamine [164]. Similarly, transition metal complexes of *p*-bromo-*N*,*N*-dimethylaniline *N*-oxide decompose within a few hours to give *p*-bromodimethylaniline and tar [167].

The complexes are generally prepared by mixing TMNO and anhydrous metal salts in non-aqueous protic polar solvents. In certain cases, dehydrating agents, such as 2,2-dimethoxypropane [142] have been employed for dehydration of hydrated metal salts. Thus, various complexes of the following general formulae: $M(TMNO)_4^{2+}$ (M = Mn [142,147], CO [142–148], Ni [142], Zn [145], Cd [145], Cu [142]); $M(TMNO)_3X^+$ (M = Co [143,147]); $M(TMNO)_2X_2$ (M = Co [142,143,146–150], Mn [143], Zn [147,151], Cd [151]); $M(TMNO)_6^{3+}$ (M = Cr [142,152], Sc [153]), $M(TMNO)X_2$ (M = Cd, Hg [151]; $M(TMNO)_2X_4$ (M = Sn, Ti, Zr [147,168]) were prepared. In addition, complexes of early transition metals, such as $MeNbOCl_2 \cdot 2TMNO$ [154], $(MeO)_5Nb(TMNO)$ [155–157], $MoO_2Cl_2 \cdot 2TMNO$ [158] and $MoO_3 \cdot 2TMNO$ [159], and of the actinides $UO_2X_2(TMNO)$ [160] and $UO_2(TMNO)_4$ [161], were also studied. The first organometallic compound containing a TMNO ligand, **XLIII**, was reported recently [162]. The N–O bond distance in **XLIV** (1.41 Å) was found to be very close to that reported for uncoordinated TMNO (1.388 Å) [169].



XLIII



XLIV

Related aliphatic amine *N*-oxide complexes, such as those of TENO [164,165,169], TPNO [164], DMEO [166] and *N*,*N*-dimethyl-*p*-bromoaniline *N*-oxide [167], were also prepared for comparison.

The *N*-oxide nitrogen is quaternary in nature and thus exhibits steric interaction with the complex formed. This steric interaction prevents the metal ions from achieving maximum coordination through the ligand alone. With the exception of Cr or Sc complexes, which coordinate six TMNO ligands, the maximum coordination number of monodentate amine *N*-oxides to a metal has been four. In addition, less strongly coordinating ligands such as Cl^- enter the coordination sphere to form a complex with the general formula $MX_2(TMNO)_2$ [142,143,146–151].

Like the majority of the metal complexes of heteroaromatic amine *N*-oxide [5–9], which are often decomposed by water, most of the aliphatic analogues are also unstable in aqueous media.

Similar to the metal complexes of heteroaromatic *N*-oxides, the coordination of TMNO and related ligands invariably occurs through the N–O oxygen. Different coordinating ability can be expected for heteroaromatic and aliphatic amine *N*-oxides, simply on the basis of their electronic structures and steric environments. It has been shown that TMNO and related aliphatic amine *N*-oxides exhibit large ligand field strengths [142,152,161].

(ii) Physical properties

(a) Infrared spectra

Direct complexation of trimethylamine-*N*-oxide and related ligands through the N–O oxygen is supported by the study of ligand IR bands. Interestingly, the N–O stretching frequency for the metal complexes formed with TMNO [142–161] and other aliphatic amine-*N*-oxides [164,165] occurs at a similar frequency to that of the free ligand [145,170,171]. It is noteworthy that a significant shift to lower frequencies was observed in the ν(NO) of heteroaromatic amine *N*-oxides upon coordination to metal ions [5–9]. This shift has been attributed to a change in the contribution of the various resonance structures of heteroaromatic amine-*N*-oxides, as a result of coordination [7,145]. Such resonance structures do not exist in TMNO and related aliphatic ligands since there is no orbital on the nitrogen atom, and thus their N–O bond has no double-bond character. This argument is consistent with the X-ray data on **XLIII** which shows that there is no change in the N–O bond distance before and after complexation of TMNO [162].

It is noteworthy that the N–O stretching vibration for DMEO shifts to lower frequencies upon coordination [166]. From the values of the N–O stretching, the divalent metal perchlorate complexes $[M(DMEO)_n](ClO_4)_2$ follow the Irving–Williams stability series: $Mn(II) < Co(II) < Na(II) < Cu(II) > Zn(II)$ [166].

The unambiguous assignment of metal–oxygen stretching frequencies is not straightforward in the case of the aliphatic amine *N*-oxide complexes. A band in the region 570–520 cm^{-1} which varies in position in different complexes has been considered primarily an M–O stretching mode [147,164]. The relatively high ν(M–O) values are in good agreement with the argument that aliphatic amine *N*-oxide is a stronger donor than trimethylphosphine oxide (with ν(M–O) at 470–400 cm^{-1}) and pyridine *N*-oxide (with ν(M–O) at 450–300 cm^{-1}) [147].

(b) Conductance

Conductivity studies in acetonitrile or nitromethane have provided structural information which is in good agreement with data suggested by other measurements. Complexes with the formula $M(TMNO)_4X_2$, where $X = ClO_4^-$, BF_4^-, NO_3^-, I^- or TsO^- are essentially 1:2 electrolytes with a tetrahedral structure, with the exception of the Cu^{II} complex, which is probably distorted square planar [142]. The conductance value for the complex $Co(TMNO)_4Br_2$ was found to be similar to that for a 1:1 electrolyte [144]. Upon addition of excess TMNO to the solution, the conductance rose to that of a 1:2 electrolyte [144].

The solution behaviour of $M(TMNO)_2X_2$ and related aliphatic amine *N*-oxide complexes has been studied in detail [143,148,164]. The complexes are non-dissociative in nature having a tetrahedral structure in solution. Addition of excess TMNO to the cobalt complexes increases the conductance values to those of 1:1 (X = Cl) and (1:2 (X = Br, I, SCN) electrolytes [143].

(c) Other properties

The electronic spectra and magnetic properties are consistent with tetrahedral stereochemistry for most ML_nX_{4-n} complexes, where L is TMNO or other aliphatic monodentate amine *N*-oxides [142–151]. The visible spectra and magnetic properties observed for the chromium complex $Cr(TMNO)_6^{3+}$ and for the DMEO analogues indicate an octahedral configuration [142,166].

Mössbauer studies on $Fe(TENO)_2X_2$ (X = Cl, Br, I) suggested a tetrahedral coordination for these complexes [165].

ACKNOWLEDGEMENT

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