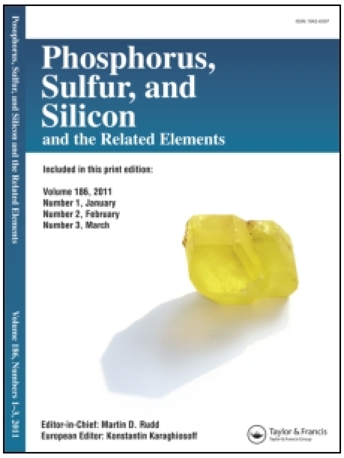
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Decisive Influence of Phosphorus Ligands on O_2 Oxidations of Alkenes in the Presence of the Iron Nitrato/Iron Nitrosyl Couple

Michèle Postel[a]; Félix Tomi[a]; Henri Li Kam Wah[a]; Laurence Mordenti[a]; Patricia Guillaume[a]
[a] Laboratoire de Chimie Moléculaire Unité Associée au C.N.R.S. n 426, Université de Nice, Nice, France

To cite this Article Postel, Michèle , Tomi, Félix , Wah, Henri Li Kam , Mordenti, Laurence and Guillaume, Patricia(1990) 'Decisive Influence of Phosphorus Ligands on O_2 Oxidations of Alkenes in the Presence of the Iron Nitrato/Iron Nitrosyl Couple', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 453 — 457

To link to this Article: DOI: 10.1080/10426509008039001

URL: http://dx.doi.org/10.1080/10426509008039001

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 453–457
Reprints available directly from the publisher
Photocopying permitted by license only

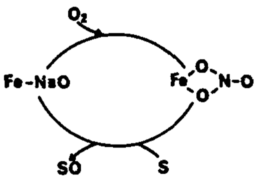
DECISIVE INFLUENCE OF PHOSPHORUS LIGANDS ON O_2 OXIDATIONS OF ALKENES IN THE PRESENCE OF THE IRON NITRATO/IRON NITROSYL COUPLE

Michèle POSTEL, Félix TOMI, Henri LI KAM WAH, Laurence MORDENTI and Patricia GUILLAUME
Laboratoire de Chimie Moléculaire[a], Unité Associée au C.N.R.S. n° 426,
Université de Nice, 06034 Nice, France.

Abstract $Fe(NO)_2XL$ and $Fe(NO)X_2L$ nitrosyl iron complexes , X = Cl, I, and L = HMPA, dppe, PPh_3, activate molecular O_2 to yield **nitrato** complexes. The phosphorous ligand is decisive for the oxidative power of these nitrates: with HMPA or dppe, oxygen transfer occurs only to phosphines. On going from HMPA to PPh_3 the single nitrato complex obtained, $Fe(NO_3)_2X(OPPh_3)_2$ **selectively epoxidizes cyclohexene**, and this is the first example of oxygen transfer from a nitrato ligand to an olefin.

INTRODUCTION

We have demonstrated that the iron-nitrato/iron nitrosyl couple constitutes a new alternative for the O_2 oxidation of alkenes.[1,2] In this system, the nitrosyl ligand, N-bonded to iron, is oxidized by O_2 into a nitrato group, bidentate, O-bonded to iron, which, in turn, transfers oxygen to alkenes or phosphines and is thus reduced to the initial N-bonded nitrosyl group (scheme 1).



In our search for the best ligand environment for such a system, we became interested in iron nitrosyl complexes with phosphorous ligands. We report here that the phosphorous ligand -triphenylphosphine (PPh_3), hexamethylphosphortriamide (HMPA), 1,2-bis(diphenylphosphino)ethane (dppe)- are decisive for the oxidative power of the Fe-NO/Fe-NO_3 couple.

RESULTS AND DISCUSSION

The Nitrosyl Complexes :

We have prepared from $[Fe(NO)_2X]_2$, X=Cl, I, a series of nitrosyl iron complexes containing PPh_3, HMPA or dppe : their nature and reactivity (scheme 2) depends upon the basicity of the phosphorous ligand.

In the presence of PPh_3, a weak donor and strong acceptor, $Fe(NO)_2X(PPh_3)$,[3] 1, are obtained. In the presence of PPh_3, these latter species lose chlorine (iodine) to yield $Fe(NO)_2(PPh_3)_2$[4] where the $Fe(NO)_2$ moiety is maintained.

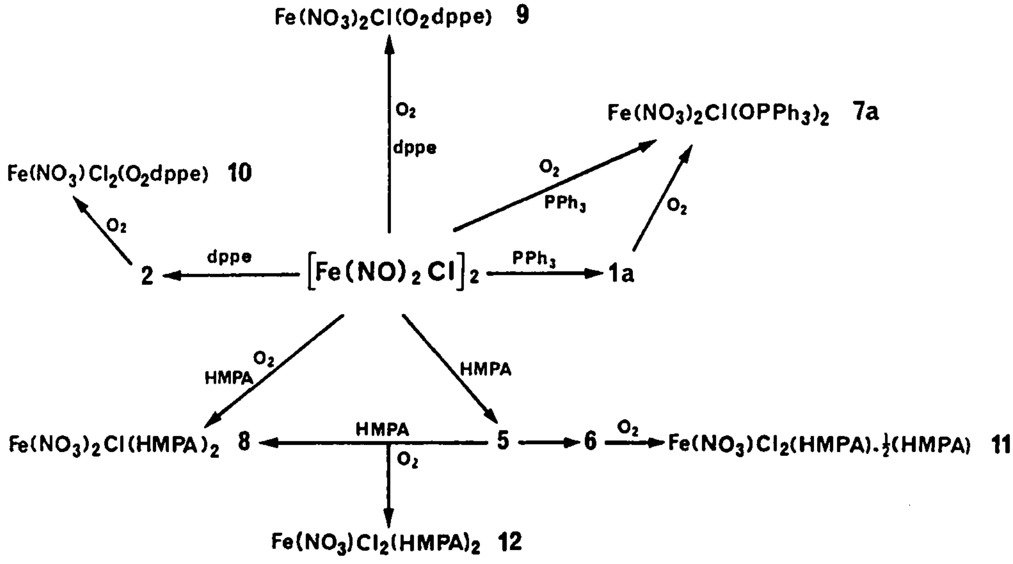
By allowing 1,2-bis(diphenylphosphino)ethane (dppe) to react with $[Fe(NO)_2(Cl)]_2$ we isolated high yields of the analogous $[Fe(NO)_2(Cl)]_2(\mu$-dppe), 2. However, when compound 2 is allowed to react further with one equivalent of dppe, besides the expected red $Fe(NO)_2(dppe)$[5,6] complex, 4, the green $Fe(NO)(Cl)_2(Odppe)$ compound, 3, is also formed.

In the case of the harder HMPA ligand, the reaction with the iron nitrosyl dimer in an argon atmosphere yielded a most unstable complex, $Fe(NO)_2(Cl)(HMPA)$, 5. To our knowledge no stable complex of iron dinitrosyl with a Fe-O-P moiety exists in the literature. In solution, 5 evolves to afford the green crystalline $Fe(NO)(Cl)_2(HMPA).\frac{1}{2}(HMPA)$, 6, together with untractable hydrated μ-oxo iron species.[7]

It is noteworthy that this transformation of 5, characterized by the loss of NO, differs from both that observed for $Fe(NO)_2(Cl)(PPh_3)$, 1, where, in the presence of PPh_3, the main route implies loss of chlorine, and for $[Fe(NO)_2Cl](\mu$-dppe), 2, where loss of both NO and Cl occurs.

Activation of Dioxygen : the $Fe\text{-}NO/Fe\text{-}NO_3$ Transformation

All these iron nitrosyl complexes were found to activate molecular O_2 to yield iron(III) nitrates and not nitrites. Furthermore, in these nitrates the phosphane ligands PPh_3 and dppe are oxidized into the corresponding oxides (scheme 2).



Oxygenation of coordinated nitric oxide by molecular oxygen generally results in the formation of nitro compounds. Furthermore, the few examples in the literature where a nitrosyl complex reacts with oxygen to form nitrato species, are concerned with cobalt,[8] iridium,[9] platinum,[10] or ruthenium[11] nitrosyl complexes which all contain the PPh_3 ligand : in the resulting nitrates, the PPh_3 ligand remains unchanged.

In the presence of triphenylphosphane, starting with $[Fe(NO)_2X]_2$ or $Fe(NO)_2Cl(PPh_3)$, **1**, a single nitrate is obtained in high yields (85%) : $Fe(NO_3)_2X(OPPh_3)_2$, **7**, where (i) both nitrosyl ligands have been oxidized into nitrates, and (ii) triphenylphosphine has been oxidized into coordinated triphenyl phosphine oxide.

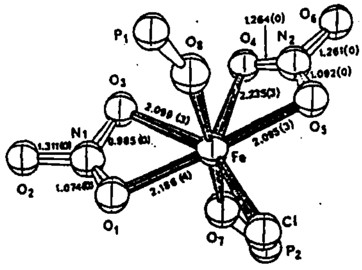
The oxygenation of $[Fe(NO)_2Cl]_2$ in the presence of HMPA or dppe (P/Fe=2/1) yielded respectively $Fe(NO_3)_2Cl(HMPA)_2$, **8**, and $Fe(NO_3)_2Cl(O_2dppe)$, **9**, where dppe has been oxidized into the corresponding dioxide. These reactions compare well with the formation of complex **7** in the presence of PPh_3.

However, HMPA and dppe induce reactivities which are in marked contrast with those observed with PPh_3.

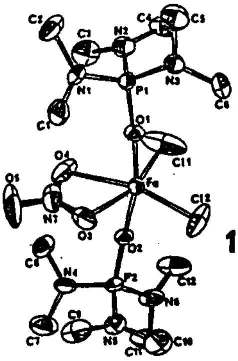
Thus, the only compound we could isolate from the direct oxidation of $[Fe(NO)_2Cl](\mu\text{-dppe})$, **2**, by O_2, was the mononitrate $Fe(NO_3)Cl_2(O_2dppe)$, **10**. Bubbling oxygen into solutions of the dinitrosyl $Fe(NO)_2Cl(HMPA)$, **5**, or mononitrosyl $Fe(NO)Cl_2(HMPA).\frac{1}{2}(HMPA)$, **6**, afforded the same yellow compound, $Fe(NO_3)(Cl)_2(HMPA).\frac{1}{2}(HMPA)$, **11**. The reaction is quantitative starting from **6** while, in the case of **5**, ca 50% of the iron is lost through decomposition into hydrated oxo species.

On the other hand, in the presence of excess HMPA, the oxygenation reaction of **5** yielded a 1/1 mixture of $Fe(NO_3)(Cl)_2(HMPA)_2$, **12**, and $Fe(NO_3)_2(Cl)(HMPA)_2$, **8**.

Molecular Structures of 7 and 12 :(figure 1)



7



12

The most striking feature in the structures of complex **7a**, $Fe(NO_3)_2Cl(OPPh_3)_2$ and 12, $Fe(NO_3)Cl_2(HMPA)_2$,, particularly in view of their use as oxygen transfer agents, is the geometry of the nitrato groups themselves. In compound 12, the iron-nitrate structural parameters are very similar to those found for other symmetrical bidentate nitrato complexes.[12] The $O_3N_7O_4$ angle involving both coordinated oxygens is less than 120 (116.0). The terminal N_7-O_5 bond (1.232(5) Å) is slightly shorter than the N-O bonds involving coordinated oxygens (1.263(5) and 1.273(6) Å).

The geometry of 7 is in marked contrast with these data. In the N_1 labelled nitrate, the internal angle is larger than 120 (124.5), and the N_1-O_2 terminal bond is surprisingly long (1.311 Å), much longer than both bridging N_1-O_1 (1.074 Å) and N_1-O_3 (0.985 Å), which is contrary to what has so far been observed in nitrato complexes.

The N_2 labelled nitrato group in 7 and all other data in the structures of 7 and 12 are conventional and compare well with the data in the literature.

Transfer of Oxygen : the Fe-NO_3 Fe-NO Reduction.

The phosphorous ligand has a decisive influence on the oxygen transfer ability of the iron nitrato complexes 7 to 12.

The pentacoordinated HMPA and O_2dppe mono-, **10** and **12**, and dinitrates, **8** and **9**, were found to react rapidly with phosphines even in the absence of oxygen.

Thus, IR monitoring of the reaction between **8** and PPh_3 (tenfold excess) under argon, in CH_2Cl_2 or CH_3CN, shows the rapid disappearance of the NO_3 vibrations in **8**, while $OPPh_3$ and coordinated NO groups become detectable : **8** is capable of transferring oxygen, and this oxygen transfer regenerates the nitrosyl moiety. Treatment of the reaction mixture afforded 4 equivalents of free $OPPh_3$, showing that 4 oxygen atoms in the dinitrato $Fe(NO_3)_2Cl(HMPA)_2$, **8**, are transferable.

$Fe(NO_3)(Cl)_2(HMPA).½(HMPA)$, **11**, has lost all oxygen transfer properties. In compound **11**, when compared with **8**, **9**, **10** or **12**, (i) the coordination sphere of the iron atom is less crowded, which should favor the coordination of the substrate, and (ii) the electron density on the metal, and therefore on the nitrato group, is lower. A key factor for an oxidizing Fe-NO/Fe-NO_3 cycle thus appears to be enhanced electron density on the nitrato group.

A most important feature of compounds **1**, $Fe(NO_3)_2Cl(OPPh_3)_2$, is that they **transfer oxygen to cyclohexene. This is the first example of oxygen transfer from a nitrato ligand to an olefin.**

When compound **1b** was kept in contact with cyclohexene (cyclohexene/Fe : 10/1) under argon at room temperature in CH_3CN solutions, cyclohexene was slowly but exclusively transformed into cyclohexene oxide. When the reaction was interrupted after 72 hrs, a 30% epoxide yield based on iron was determined; none of the usual other oxidation products of cyclohexene (e.g. cyclohexenone, cyclohexenol...) could be detected in the GLC/MS analysis.

We take these results to further support our hypothesis that the Fe-NO/Fe-NO_3 redox couple inherently constitutes an alternative for the O_2 oxidation of organic substrates if the appropriate ligand environment can be designed. The Fe(NO_3) Fe(NO) transformation, i.e. the oxygen transfer step, is obviously the most demanding.

ACKNOWLEDGEMENTS

We wish to thank M. Pierrot and A. Baldy of the Laboratoire de Cristallochimie of the University of Aix-Marseille III for performing the X-ray study. We are grateful to the Centre National de la Recherche Scientifique for financial support of this work.

REFERENCES

1. F. Tomi, H. Li Kam Wah, and M. Postel, New J. Chem., **12**, 289, (1988).
2. H. Li Kam Wah, M. Postel, and F. Tomi, Inorg. Chem. **28**, 233 (1989).
3. J. Kopf, and J. Schmidt, Z. Naturforsch. **30b**, 149 (1975).
4. S. Pignataro, G. Distefano, and A. Foffani, J. Am. Chem. Soc. **92**, 6425 (1970).
5. D. W. Mc.Bride, S. L. Stafford, and F. G. A. Stone, Inorg. Chem. **1**, 386 (1962).
6. R. J. Mawby, D. Morris, E. M. Thorteinson, and F. Basolo, Inorg. Chem. **5**, 27 (1966).
7. K. Nakamoto, "Infra-red and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed. (Wiley-Interscience, New York, 1978), pp 244-247.
8. W. C. Trogler, and L. G. Marzilli, Inorg. Chem., **13**, 1008 (1974).
9. M. Kubota, and D. A. Phillips, J. Am. Chem. Soc., **97**, 5637 (1975).
10. S. A. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Segal, R. Walters, and C. Zuccaro, J. Chem. Soc. Dalton, 1981, 234.
11. K. R. Grundy, K. R. Laing, and W. R. Roper Chem. Commun., 1970, 1500.
12. C. C. Addison, N. Logan, S. C. Wallwork, and C. Garner, Q. Rev. Chem. Soc., **25**, 289 (1971).*