

## Coordination Chemistry of C-Nitroso-compounds

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### 1 Introduction

The chemistry of C-nitroso-compounds commenced in 1874 with the synthesis of *p*-nitrosodimethylaniline<sup>1</sup> (NODMA) and of nitrosobenzene<sup>2</sup> (NOB). It was not until the 1960s, however, that the coordination chemistry of C-nitroso-compounds began to be explored in detail, and relatively few coordination compounds were reported before 1950. The chemistry of C-nitroso-compounds has been actively investigated from the time of the first synthesis and has been successively reviewed from 1903 onwards<sup>3–8</sup> without attention being directed to the potential of nitroso-compounds for coordinating to metals.

A few early references to coordination compounds of NOB and NODMA are to be found in the literature, beginning with Pickard and Kenyon<sup>9</sup> in 1907 who claimed the preparation of (NOB)<sub>5</sub>.CdI<sub>2</sub> and (NODMA)<sub>2</sub>.ZnCl<sub>2</sub> by direct addition of alcoholic solutions of the components. Baudisch<sup>10,11</sup> interacted NOB and the hexacyanoferrate(II) anion to form (NOB)Fe(CN)<sub>3</sub><sup>3-</sup>, which was present in solution. Other NOB complexes with titanium and tin tetrachlorides (MCl<sub>4</sub>.NOB) were prepared in 1927<sup>12</sup> and a series of uranyl complexes with NODMA and *p*-nitrosodiethylaniline (NODEA) containing the ions UO<sub>2</sub><sup>2+</sup> (NODMA)<sub>n</sub> and UO<sub>2</sub><sup>2+</sup> (NODEA)<sub>n</sub> (*n* = 1 or 2) were first prepared in 1933.<sup>13</sup> In 1965, Gustorf and Jun<sup>14</sup> drew attention to the formation of an unanalysed solid

\* To whom correspondence should be addressed.

<sup>1</sup> A. Baeyer and H. Caro, *Ber.*, 1874, 7, 809.

<sup>2</sup> A. Baeyer, *Ber.*, 1874, 7, 1638.

<sup>3</sup> J. Schmidt, 'Sammlung chemischer und chemisch-technischer Vorträge', Vol. 8, Chapter 11, ed. F. B. Ahrens, Enke, Stuttgart, 1903.

<sup>4</sup> N. V. Sidgwick, 'The Organic Chemistry of Nitrogen', Clarendon Press, Oxford, 1937, p. 204.

<sup>5</sup> B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, 12, 321.

<sup>6</sup> P. A. S. Smith, 'The Chemistry of Open-Chain Organic Nitrogen Compounds', Vol. 2, Benjamin, New York, 1966, p. 355.

<sup>7</sup> 'The Chemistry of the Nitro and Nitroso Groups, Part I', ed. H. Feuer, Interscience, New York, 1969.

<sup>8</sup> 'Houben Weyl, Methoden der organischen Chemie', Band X/1, Stickstoff-Verbindungen, ed. E. Müller, Thieme, Stuttgart, 1971.

<sup>9</sup> R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1907, 91, 896.

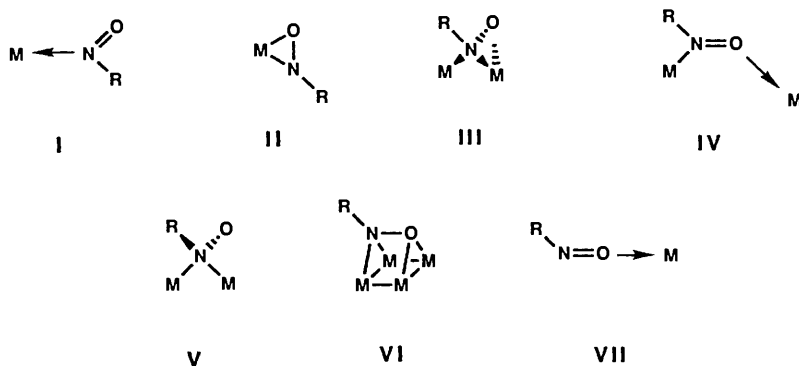
<sup>10</sup> O. Baudisch, *Ber.*, 1921, 54, 413.

<sup>11</sup> O. Baudisch, *Ber.*, 1929, 62, 2706.

<sup>12</sup> H. Reihlen and A. Hake, *Justus Liebig's Ann. Chem.*, 1927, 452, 47.

<sup>13</sup> R. Rascanu, *Ann. Sci. Univ. Jassy*, 1933, 10, 130.

<sup>14</sup> E. K. Gustorf and M.-J. Jun, *Z. Naturforsch. B.*, 1965, 20, 521.



Scheme 1

resulting from the exposure to light of a solution of iron pentacarbonyl in nitrobenzene<sup>15</sup> They suggested that, by comparison with their own detailed studies, it was probable that Dewar and Jones had prepared  $[\text{NOB Fe}(\text{CO})_3]_2$  and that this was therefore the first example of a C-nitroso-compound coordinated to a metal

## 2 Synthesis of Complexes of C-Nitroso-compounds

It is necessary to anticipate the structural studies of the coordination chemistry by making use of the classification<sup>16 17</sup> of the seven different bonding types exhibited by monomeric C-nitroso-compounds as reported in Scheme 1 Such a classification assists our understanding of the synthetic routes available

**A. Preparation of Complexes of Types I, III, and VII by Direct Addition of the Partners and without Ligand Displacement.**—Most of the early preparations listed above<sup>9 12 13</sup> employed this simple preparative technique It has been frequently employed for preparation of NODMA complexes [equation 1, where  $\text{M} = \text{Co},^{18} \text{Ni},^{19} \text{Pd},^{20 21} \text{Cd},^{22} \text{Zn},^{23}$  and  $(\text{CH}_3)_2\text{Sn}^{24}$ ] The donor strength of the nitroso-group is markedly increased by substitution in the *para* position of the benzene ring of a strongly electron-donating group

<sup>15</sup> J Dewar and H O Jones *Proc Roy Soc A* 1905 **76**, 558

<sup>16</sup> R S Pilato C McGettigan G L Geoffroy A L Rheingold and S J Geib *Organometallics* 1990 **9** 312

<sup>17</sup> M Cameron B G Gowenlock and G Vasapollo *J Organomet Chem* 1991 in press

<sup>18</sup> D M Sams and R J Doedens *Inorg Chem* 1979 **18** 153

<sup>19</sup> C J Popp and R O Ragsdale *Inorg Chem* 1968 **7** 1845

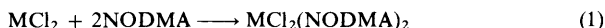
<sup>20</sup> I Batten and K E Johnson *Can J Chem* 1969 **47** 3075

<sup>21</sup> A S Pilipenko L L Shevchenko and A P Popel *Zh Priklad Spectrosk* 1976 **24** 365

<sup>22</sup> P O Ikekwere and K E Johnson *Synth React Inorg Met Org Chem* 1985 **15** 883

<sup>23</sup> P O Ikekwere *Synth React Inorg Met Org Chem* 1988 **18** 629

<sup>24</sup> G Matsubayashi and K Nakatsu *Inorg Chim Acta* 1982 **64** L163



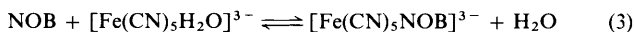
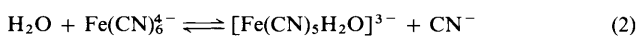
Other *p*-nitrosoaniline derivatives of Ni, Co, and Cu have been similarly prepared.<sup>25</sup> A range of uranyl complexes with NODMA are also made by direct addition,<sup>26</sup> as are the corresponding lanthanide complexes  $\text{MX}_3(\text{NODMA})_3$  ( $\text{M} = \text{La, Ce, Pr, Nd, Sm, Ho, Er, Tm}$ ;  $\text{X} = \text{Cl, NO}_3$ ).<sup>27</sup>

A further example of coordination by direct addition is provided by the reaction of a range of substituted nitrosobenzenes with ferrohaemoglobin under anaerobic conditions.<sup>28</sup> In these type I coordinations it is noteworthy that coordination is completely inhibited by an *ortho* *t*-butyl group but not by smaller *ortho* alkyl groups, also by a pair of *ortho* methyl groups, chlorine or bromine atoms, but not by a pair of the same substituents elsewhere on the benzene ring. Such effects are clearly compatible with steric hindrance preventing  $\sigma$ -N (type I) coordination.

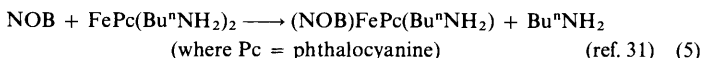
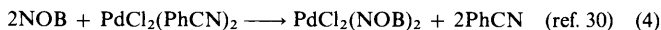
In a recent paper<sup>28a</sup> it has been reported that NOB inserts into  $[\text{Cp}^*\text{Rh}(\mu\text{-Cl})_2]$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ), the  $\text{Rh}^{\text{II}}$  dimer having a reactive Rh–Rh bond and a type III complex results.

### B. Preparation of Complexes of Types I, II, III by Direct Addition of the Nitroso-compound to a Coordination Compound accompanied by Ligand Displacement.—

In contrast to method A which is primarily applicable to NODMA complexes, the ligand displacement syntheses are primarily used for NOB, substituted NOB, 2-methyl-2-nitrosopropane, and trifluoronitrosomethane complexes. The first use of this technique is provided by the Baudisch reaction<sup>10</sup> between the hexacyanoferrate(II) ion and nitrosobenzene which follows the mechanism<sup>29</sup> shown in reactions 2 and 3.



The method has been used for a variety of type I complexes as illustrated in equations 4–15.



<sup>25</sup> C. J. Popp and R. O. Ragsdale, *J. Chem. Soc. A*, 1970, 1822.

<sup>26</sup> G. Condorelli, I. Fragala, and S. Giuffrida, *J. Inorg. Nucl. Chem.*, 1975, **37**, 1177.

<sup>27</sup> A. Seminara, *Boll. Sedute Accad. Gioenia Sci. Nature Catania*, 1969 [4], **10**, 147. *Chem. Abstr.*, 1971, **74**, 71 050.

<sup>28</sup> K. Hirota and H. A. Itano, *J. Biol. Chem.*, 1978, **253**, 3477.

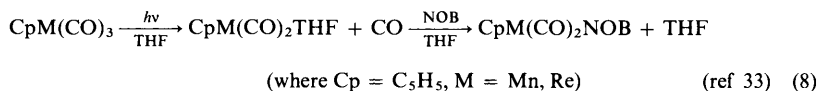
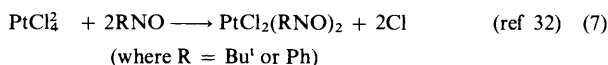
<sup>28a</sup> P. R. Sharp, D. W. Hoard, and C. L. Barnes, *J. Am. Chem. Soc.*, 1990, **112**, 2024.

<sup>29</sup> D. Pavlovic, I. Murati, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 1973, 602.

<sup>30</sup> A. L. Balch and D. Petridis, *Inorg. Chem.*, 1969, **8** 2247.

<sup>31</sup> J. J. Watkins and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2720.

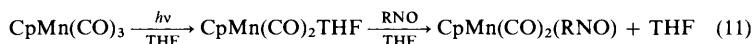
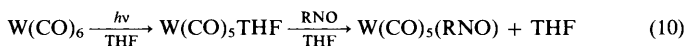
*Coordination Chemistry of C-Nitroso-compounds*



[where R = C<sub>6</sub>H<sub>5</sub>, *p*-BrC<sub>6</sub>H<sub>4</sub>, M = Rh, Ir, diene = cyclooctadiene (COD) or norbornadiene (NBD)]

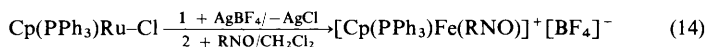
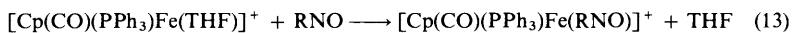
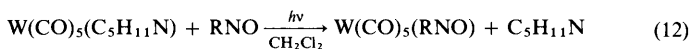
An extension<sup>35</sup> of reaction 9 leads to further complexes such as RuCl<sub>2</sub>(COD)-(NOB)<sub>2</sub>, RuCl<sub>2</sub>(DMSO)<sub>2</sub>(NOB)<sub>2</sub>, PdCl<sub>2</sub>L<sub>2</sub> (where L = *para*-substituted NOB), PtCl<sub>2</sub>(*p*-Me C<sub>6</sub>H<sub>4</sub> NO)<sub>2</sub>, and RhCl(CO)<sub>2</sub>(NOB)

Reaction 8 has been extended by Link<sup>36</sup> to some tungsten complexes (reaction 10) and manganese complexes (reaction 11)



[where R = *t*-C<sub>4</sub>H<sub>9</sub>, neo-C<sub>5</sub>H<sub>11</sub>CM<sub>2</sub>, cyclo-C<sub>3</sub>H<sub>5</sub> (reaction 10 only), 1-adamantyl]

These reactions have been further extended<sup>16</sup>



<sup>32</sup> D Mansuy, M Drème, J C Clottard, and J Guilhem, *J Organomet Chem*, 1978, **161**, 207

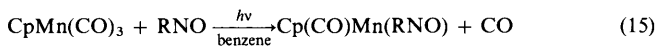
<sup>33</sup> V N Setkina, S P Dolgova, D V Zagorevskii, V F Sizoi, and D N Kursanov, *Bull Acad Sci USSR Chem Ser*, 1982, 1239

<sup>34</sup> G Vasapollo, P Giannocaro, C F Nobile, and F Allegretta, *J Organomet Chem*, 1984 **270** 109

<sup>35</sup> (a) G Vasapollo, C F Nobile, P Giannocaro, and F Allegretta, *J Organomet Chem* 1984 **277** 417

(b) H Alper and G Vasapollo, *Tetrahedron Lett*, 1987, **28**, 6411

<sup>36</sup> M Link, Doctoral Thesis, University of Hamburg, 1988

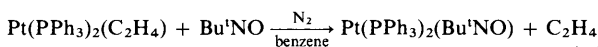
(where R = t-C<sub>4</sub>H<sub>9</sub>)

Vasapollo's reaction (9) has been extended<sup>37</sup> to a NODMA complex where M = Rh, diene = COD.

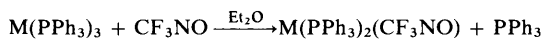
The range of this preparative method is exemplified by the preparation of type II complexes (reactions 16—20) and type III complexes (reactions 21—22).

(where n = 2 or 4 and R = p-X.C<sub>6</sub>H<sub>4</sub>, X = Me<sub>2</sub>N, MeO, Me, H, Cl, Br) (ref. 38) (16)

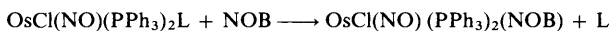
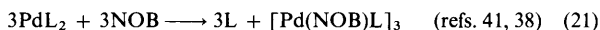
(where M = Ni, Pd, Pt) (ref. 38) (17)



(ref. 39) (18)



(where M = Pt, Pd) (ref. 39) (19)

(where L = C<sub>2</sub>H<sub>4</sub> or PPh<sub>3</sub>) (ref. 40) (20)(where L = PBU<sub>3</sub>, PPhBu<sub>2</sub>)

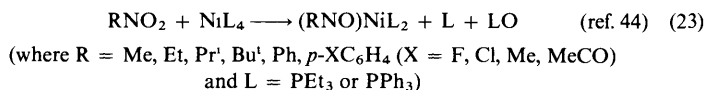
(ref. 42) (22)

### C. Preparations of Complexes of Types I, III, IV, V, VI using Nitro-compounds as the Source of the RNO Group.—(i) Without Irradiation.

The only example known of a type VI complex is prepared from the reaction of tri-iron dodecacarbonyl with nitroethane<sup>43</sup> to give a nitrene-nitroso-complex of formula Fe<sub>4</sub>(CO)<sub>11</sub>-(NEt)(ONEt).

Nickel(o) phosphine complexes react with a variety of aliphatic and aromatic nitro-compounds according to the overall equation 23.

<sup>37</sup> G. Matsubayashi and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1990, 437.<sup>38</sup> S. Otsuka, Y. Aotani, Y. Tatsuno, and T. Yoshida, *Inorg. Chem.*, 1976, **15**, 656.<sup>39</sup> M. Pizzotti, F. Porta, S. Cenini, F. Demartin, and N. Masciocchi, *J. Organomet. Chem.*, 1987, **330**, 265.<sup>40</sup> M. Herberhold and A. F. Hill, *J. Organomet. Chem.*, 1989, **363**, 371.<sup>41</sup> M. Calligaris, T. Yoshida, and S. Otsuka, *Inorg. Chim. Acta*, 1974, **11**, L15.<sup>42</sup> S. Stella, C. Floriani, A. Chiesa-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1988, 545.<sup>43</sup> G. Gervasio, R. Rossetti, and P. L. Stanghellini, *J. Chem. Soc., Chem. Commun.*, 1977, 387; *J. Chem. Res. (M)*, 1979, 3943.



The mechanism below (reactions 24—6) has reaction 25 as the rate determining step:



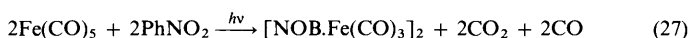
These nickel complexes have a type II structure.

Nitrobenzene reacts rapidly<sup>45</sup> with the molybdenum complex Mo(CO)<sub>2</sub>-(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> in dichloroethane to give MoO(NO)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>. This complex can be reduced by triphenyl phosphine to give the type II complex Mo(NO)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>.

Further molybdenum complexes, MoO<sub>2</sub>(RNO), where R = Ph, Me, *o*-MeC<sub>6</sub>H<sub>4</sub> can be obtained from refluxing molybdenum hexacarbonyl and the nitro-compound under nitrogen.<sup>46</sup>

An intriguing NOB complex was prepared<sup>47</sup> in an attempt to reduce nitrobenzene to aniline with a highly reactive catalyst, PtH<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>. The resultant complex, Pt<sub>2</sub>(NOB)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub>, is unusual in that it displays three different coordination modes, namely types I, IV, and V.

(ii) *With Irradiation.* A type III complex is prepared from irradiation of iron pentacarbonyl in nitrobenzene<sup>14</sup> or substituted nitrobenzene<sup>48</sup> using either light or  $\gamma$ -rays according to reaction 27.



**D. Preparation from Imido-complexes.**—This synthetic route has been applied solely to rhenium complexes and the direct oxygenation route is illustrated in equation 28.<sup>49</sup>

An alternative oxidation route for the second of these imido complexes is available using *p*-nitrotoluene at 80—90 °C as the oxidant, the other product being *p*-toluidine. The nitroso-complexes formed are presumed to be type I.

<sup>44</sup> R S Berman and J K Kochi, *Inorg Chem*, 1980, **19**, 248

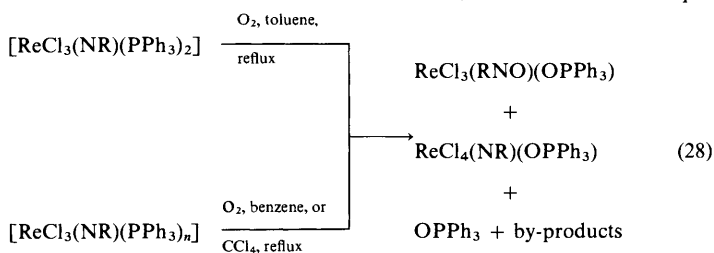
<sup>45</sup> E A Maatta and R A D Wentworth, *Inorg Chem*, 1980, **19**, 2597

<sup>46</sup> A R Middleton and G Wilkinson, *J Chem Soc, Dalton Trans.* 1981, 1898

<sup>47</sup> D L Packett, W C Trogler, and A L Rheingold, *Inorg Chem*, 1987, **26**, 4309

<sup>48</sup> E K Gustorf, M C Henry, R E Sacher, and C Di Petro, *Z Naturforsch B*, 1966, **21**, 1152

<sup>49</sup> G La Monica and S Cenini, *Inorg Chim Acta*, 1978, **29**, 183, *J Chem Soc, Dalton Trans.* 1980, 1145



(R = *p*-X.C<sub>6</sub>H<sub>4</sub> where X = H, MeO, Me)

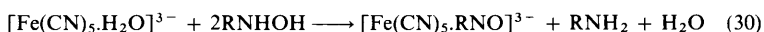
It would be of considerable interest to extend this reaction to other imido complexes.

**E. Preparation from Hydroxylamines.**—Type II complexes of molybdenum<sup>50,51</sup> and tungsten<sup>51</sup> have been prepared by reaction of metal oxo-containing compounds (M=O) with aryl<sup>50,51</sup> and *N*-*t*-butyl hydroxylamine according to the general reaction (29).



and Scheme 2 illustrates the products obtained.

Several other preparations have been reported. The essential feature is the oxidation of the hydroxylamine followed by coordination of the nitroso-compound. Waters<sup>52</sup> has extended the range of Baudisch complexes [Fe<sup>II</sup>(CN)<sub>5</sub>.RNO]<sup>3-</sup> by utilising the reaction of aqueous sodium aquapentacyanoferrate (3-) with alkyl and aryl hydroxylamines at controlled pH ranges. The reaction (30) represents the overall process.



It has long been known that nitrosoarenes bind to haemoglobin<sup>53,54</sup> and Mansuy and co-workers<sup>55,56</sup> have shown that nitrosoalkane complexes of myoglobin, haemoglobin, and cytochrome P-450 are formed during the oxidation of *N*-alkylhydroxylamines in the presence of these haemoproteins, and have extended the method to porphyrins<sup>57</sup> whilst Lindeke<sup>58</sup> has suggested a mechanism (reaction 31) to account for the observations.

<sup>50</sup> L. S. Liebeskind, K. B. Sharpless, R. D. Wilson, and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 7061.

<sup>51</sup> D. A. Muccigrosso, S. E. Jacobson, P. A. Apgar, and F. Mares, *J. Am. Chem. Soc.*, 1978, **100**, 7063.

<sup>52</sup> W. A. Waters, *J. Chem. Soc., Perkin Trans. 2*, 1976, 732.

<sup>53</sup> F. Jung, *Biochem. Z.*, 1940, **305**, 248.

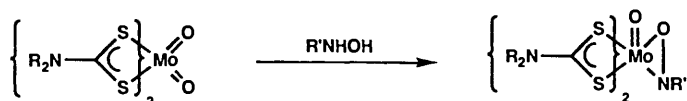
<sup>54</sup> D. Keilin and E. F. Hartree, *Nature*, 1943, **151**, 390.

<sup>55</sup> D. Mansuy, P. Beaune, J. C. Chottard, J. F. Bartoli, and P. Gans, *Biochem. Pharmacol.*, 1976, **25**, 609.

<sup>56</sup> D. Mansuy, J. C. Chottard, J. F. Bartoli, and P. Gans, *Eur. J. Biochem.*, 1977, **76**, 607.

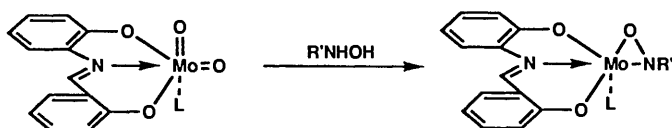
<sup>57</sup> D. Mansuy, J. C. Chottard and M. Lange, *J. Am. Chem. Soc.*, 1977, **99**, 6441.

<sup>58</sup> B. Lindeke, *Drug Metabolism Reviews*, 1982, **13**, 71.

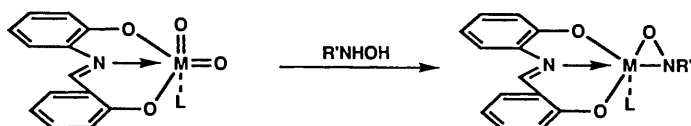


$R = \text{Me}$        $R' = \text{tBu, Ph, 4-ClC}_6\text{H}_4, 4\text{-CNC}_6\text{H}_4$

$R = \text{Et}$        $R' = \text{Ph}$



$R' = \text{tBu, Ph, 4-ClC}_6\text{H}_4, 4\text{-CNC}_6\text{H}_4$



$M = \text{Mo}$        $L = \text{HMPT}$

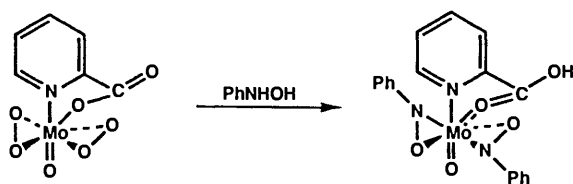
$R' = \text{tBu, Ph, 4-ClC}_6\text{H}_4, 4\text{-CNC}_6\text{H}_4$

$M = \text{Mo}$        $L = \text{C}_5\text{H}_5\text{N}$

$R' = \text{Ph}$

$M = \text{W}$        $L = \text{HMPT}$

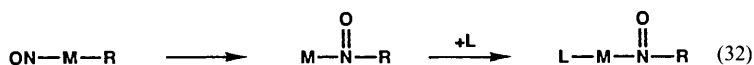
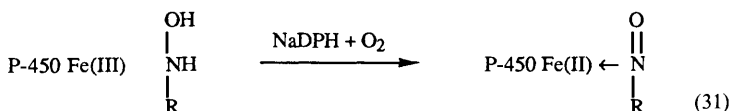
$R' = \text{Ph}$



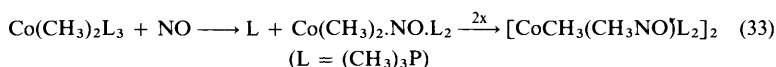
Scheme 2

**F. Nitrosyl Migration Reactions.**—An overall reaction scheme for the varied range of such migration reactions is given in reaction 32.



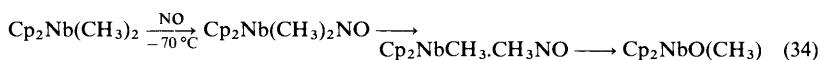


There are a variety of syntheses reported in the literature of which the systems using nitric oxide as a reagent deserve first mention. Klein and Karsch<sup>59</sup> prepared the pentacoordinated  $d^7$ -complex  $\text{Co}(\text{CH}_3)_2(\text{P}(\text{CH}_3)_3)_3$  which reacted with nitric oxide according to equation 33.



where the resultant dinuclear complex exhibits type III coordination.

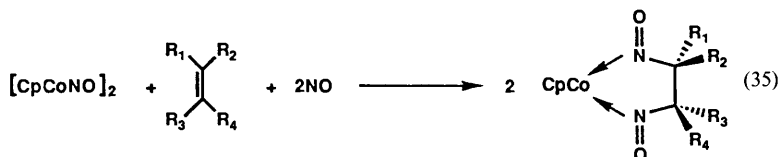
Middleton and Wilkinson<sup>60</sup> presented evidence for a type II nitrosomethane complex as an intermediate in the reaction sequence shown in equation 34.



They extended the range of complexes produced<sup>46</sup> from reaction of nitric oxide with transition metal methyls obtaining both type II complexes of rhenium, chromium, and molybdenum, and type III complexes of cobalt and molybdenum. In addition a rhenium type II complex of the previously unknown nitroso-trimethylsilylmethane was obtained.

In 1973, Brunner and Loskot<sup>61</sup> prepared the first complexes of di-nitroso-compounds from reaction of cyclopentadienyl cobalt carbonyls or nitrosyls with nitric oxide and alkenes of the norbornene type.

These syntheses of type I complexes were further extended by Bergman *et al.* They showed that unstrained alkenes could form complexes<sup>62</sup> of dinitrosoalkanes (reaction 35).

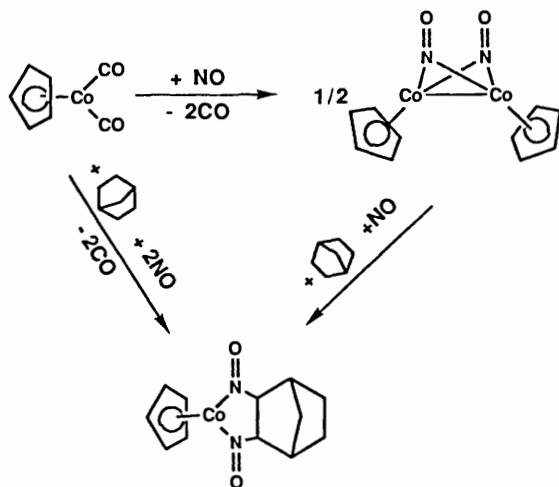


<sup>59</sup> H.-F. Klein and H. H. Karsch, *Chem. Ber.*, 1976, **109**, 1453.

<sup>60</sup> A. R. Middleton and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1980, 1888.

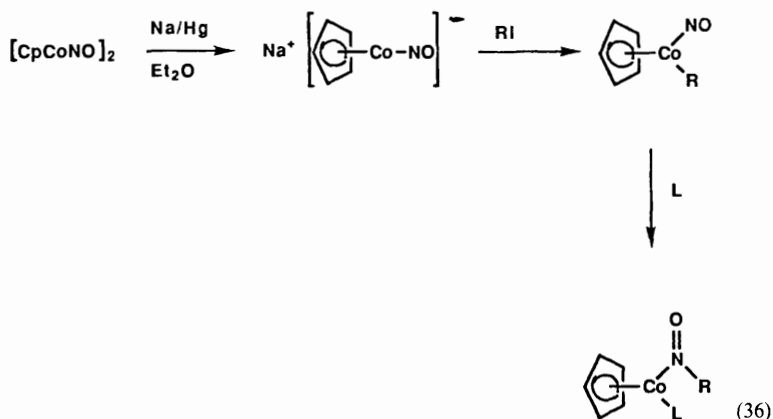
<sup>61</sup> H. Brunner and S. Loskot, *J. Organomet. Chem.*, 1973, **61**, 401.

<sup>62</sup> P. N. Becker and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 2985; *Organometallics*, 1983, **2**, 787.



Scheme 3

Further studies<sup>63</sup> of the migratory insertion of coordinated nitric oxide into Co-C bonds use the reaction sequence (36) to form type I nitrosoalkane complexes [where L = PPh<sub>3</sub> and R = CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CH, and *p*-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>].

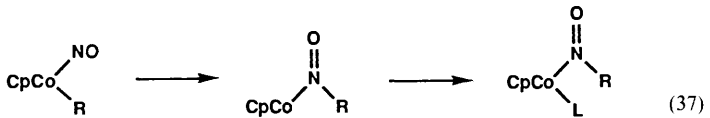


The accompanying kinetic investigations by the authors establish the intermediacy of the nitrosyl compound CpCo(NO)R and the sequence given in reaction 37.

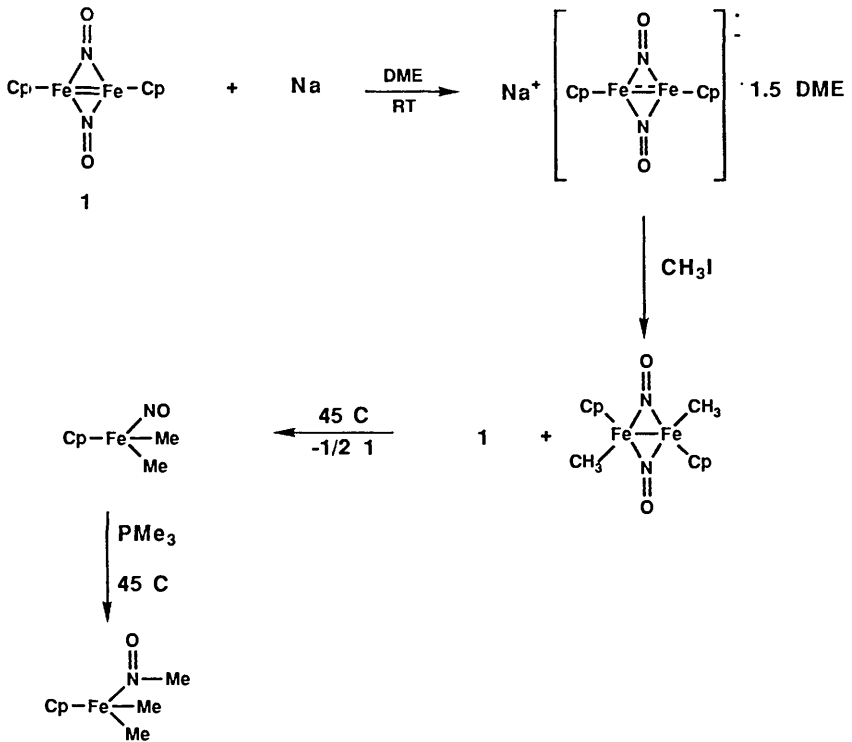
A similar reaction system occurs<sup>64</sup> when cyclopentadienylnitrosyl iron dimer

<sup>63</sup> W. P. Weiner and R. G. Bergman, *J. Am. Chem. Soc.*, 1983, **105**, 3922.

<sup>64</sup> M. D. Seidler and R. G. Bergman, *Organometallics*, 1983, **2**, 1897.



is reduced with sodium in dimethoxyethane and the resulting radical anion salt is doubly methylated. Rearrangement of the product leads to a monomeric cyclopentadienyl dimethyl nitrosyl iron which undergoes migratory insertion of NO in the presence of trimethyl phosphine (Scheme 4).



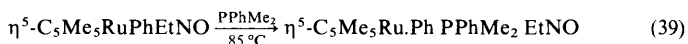
Scheme 4

A similar migratory insertion of NO into the metal-carbon bond in the presence of trimethylphosphine has been reported<sup>65</sup> for pentamethyl cyclopentadienyl dimethyl nitrosyl iron.

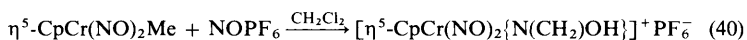


<sup>65</sup> B N Diel, *J. Organomet. Chem.*, 1985, **284**, 257

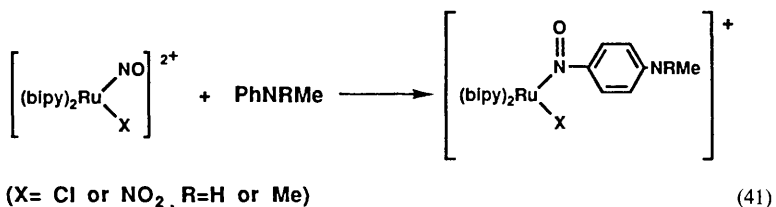
Extension to ruthenium complexes has been established<sup>66</sup> (reaction 40).



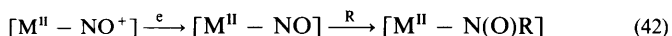
The insertion of the nitrosonium ion into a Cr-CH<sub>3</sub> bond (reaction 40) to give a formaldoxime complex<sup>67</sup> is presumed to involve the type I nitrosomethane complex as an intermediate.



**G. Electrophilic Substitution in Aromatic Systems by Co-ordinated Nitrosyl.**—The coordinated nitrosyl group in Ru(bipy)<sub>2</sub>(NO)X<sup>2+</sup> can function as an electrophile in aromatic substitution reactions (41) with activated arenes such as *N*-methyl and *N,N*-dimethylaniline leading to type I complexes<sup>68</sup> of the *p*-substituted nitrosoarenes.



**H. Radiation Syntheses.**—Hoffman has utilised one-electron reduction of deoxygenated aqueous solutions of metal-nitrosyl coordinated compounds of ruthenium<sup>69,71</sup> and iron<sup>70,71</sup> in the presence of organic compounds (RH) using both continuous and pulse radiolysis. The radiolysis of the neutral aqueous solutions produces e<sub>aq</sub><sup>-</sup>, ·OH, and H· and the two latter species produce the organic radical R· by H-abstraction from RH. The general synthetic route [reaction 42, where M<sup>II</sup> = Fe(CN)<sub>3</sub><sup>3-</sup>, Ru(NH<sub>3</sub>)<sub>2</sub><sup>3+</sup>, and R· = ·CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>OH, ·CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>NH<sub>3</sub><sup>+</sup>, ·CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CO<sub>2</sub><sup>-</sup>, ·CH<sub>2</sub>C(CH<sub>3</sub>)(NH<sub>3</sub><sup>+</sup>)CO<sub>2</sub><sup>-</sup>, ·CH<sub>2</sub>C(CH<sub>3</sub>)(OH)CO<sub>2</sub><sup>-</sup>, ·CH<sub>2</sub>(CH<sub>3</sub>)NC(O)CH<sub>3</sub>] takes place giving type I complexes.



<sup>66</sup> J Chang, M D Seidler, and R G Bergman, *J Am Chem Soc*, 1989, **111**, 3258

<sup>67</sup> P Legzdins, B Wassink, F W B Einstein, and A C Willis, *J Am Chem Soc*, 1986, **108**, 317

<sup>68</sup> W L Bowden, W F Little, and T J Meyer, *J Am Chem Soc*, 1974, **96**, 5605, 1976, **98**, 444

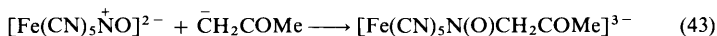
<sup>69</sup> J N Armor, R Furman, and M Z Hoffman, *J Am Chem Soc*, 1975, **97**, 1737

<sup>70</sup> R P Cheney, M G Simic, M Z Hoffman, I A Taub, and K-D Asmus, *Inorg Chem*, 1977, **16**, 2187

<sup>71</sup> R P Cheney, S D Pell, and M Z Hoffman, *J Inorg Nucl Chem*, 1979, **41**, 489

The ruthenium complexes were sufficiently stable to be isolated, as the tetraphenyl borate salts. Similarly the sodium salt,  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}]$  could also be isolated.

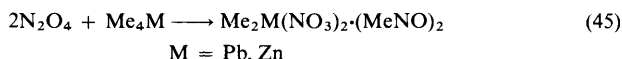
**I. Other Synthetic Routes to Short-lived Complexes.**—Waters<sup>52</sup> has drawn attention to the Legal complexes<sup>72</sup> arising from reaction of the carbanion of acetone and also from the carbanions of other aliphatic aldehydes and ketones (reaction 43). These complexes are relatively short-lived and liberate the isomeric oximino-compound.<sup>73</sup>



The reaction of benzyl bromide with various nitrosyl ruthenium complexes gives benzaldoxime as a final product<sup>74</sup> and initial formation of phenyl-nitrosomethane complexes by reaction 44 is suggested to occur prior to isomerization to the oxime complex.



**J. Complexes of Dimeric Nitroso-Compounds.**—There are very few reports of the formation of such compounds but three examples are of interest. Gaseous dinitrogen tetroxide when bubbled into an ethereal solution of tetramethyl lead<sup>75</sup> or into a cooled ethyl acetate solution of tetramethyl tin<sup>76</sup> produces a 1:1 complex of the *cis*-dimer of nitrosomethane with dimethyl metal dinitrate (45).



Reduction of 1,2,3-trimethoxy-5-nitrobenzene with aqueous ethanolic ammonium chloride and zinc powder and a controlled amount of nitrous acid produced a white solid claimed to be a 1:1 complex of dimeric 1,2,3-tri-methoxy-5-nitrosobenzene and zinc nitrite.<sup>77</sup>

### 3 Reactions of Coordinated Nitroso-compounds

It is well known<sup>5-8</sup> that *C*-nitroso-compounds exhibit a wide range of reactions and it is of interest to note whether coordination to metals results in any change in the patterns of these reactions and whether there are reactions that are characteristic of the coordination mode. Wherever  $\pi$ -NO coordination is participating (types II, III, IV, VI) it is to be expected that the weakening of the

<sup>72</sup> N. V. Sidgwick, 'Chemical Elements and their Compounds', Clarendon, Oxford, 1950, Vol. 2, p. 1345.

<sup>73</sup> L. Cambi, A. Cagnasso, and T. Ricci, *Chem. Abstr.*, 1931, **25**, 2383.

<sup>74</sup> J. A. McCleverty, C. W. Ninnes, and I. Wolochowicz, *J. Chem. Soc., Dalton Trans.*, 1986, 743.

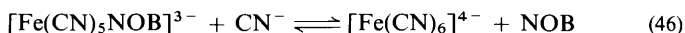
<sup>75</sup> K. C. Williams and D. W. Imhoff, *J. Organomet. Chem.*, 1972, **42**, 107.

<sup>76</sup> K. C. Williams and D. W. Imhoff, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 227.

<sup>77</sup> H. I. Bolker and F. L. Kung, *J. Chem. Soc.*, 1969, 2298.

bonding between N and O may lead to new reaction pathways. The following survey of reactions is necessarily selective and we have classified the reactions into nine major areas.

**A. Displacement of RNO Ligand.**—It is to be expected that nitroso-compounds may be displaced from a complex by another molecule that can be bonded more strongly to the metal centre. Examples include the displacement of NOB from a Baudisch complex by cyanide ion <sup>78</sup> (reaction 46).

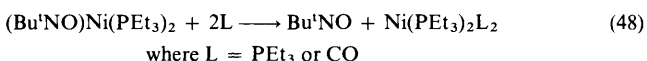


which has been shown to proceed by a complex mechanism with an initial *S<sub>N</sub>1* dissociation step (reaction 47),



and the displacement of NOB from Rh(COD)(NOB) by triphenylphosphine.<sup>34</sup>

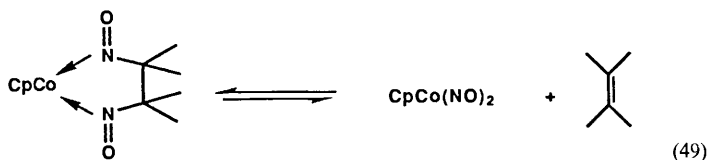
Many complexes are highly stable in the presence of other ligands, *e.g.* it has been shown<sup>62</sup> that cobalt dinitrosoalkane complexes are inert to carbon monoxide and to trimethylphosphine. On the other hand some type II nickel complexes can undergo ligand displacement relatively rapidly.<sup>44</sup>



The complex W(CO)<sub>5</sub>NOB undergoes slow ligand displacement when dissolved in acetonitrile.<sup>33</sup>

The complex W(CO)<sub>5</sub>Bu<sup>t</sup>NO is stable to carbon monoxide, triphenylphosphine, and *t*-butyl-isocyanide in methylene chloride although the same complex undergoes rapid ligand displacement by solvent in acetone and THF solution.<sup>16</sup>

**B. Reversible Exchange with Alkenes.**—Becker and Bergman<sup>62</sup> have shown that thermal exchange of alkenes in cyclopentadienyl cobalt dinitrosoalkane complexes can occur and that this is dependent upon the dissociation reaction 49.



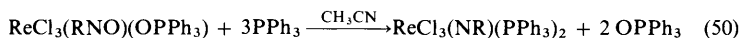
**C. Thermal Decomposition of Complexes.**—There are wide variations in the thermal stability of the complexes. Watkins and Balch<sup>31</sup> showed that the rate of

<sup>78</sup> D. Pavlovic, I. Murati, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 1973, 602.

exchange between free and complexed nitrosotoluene in a ferrous phthalocyanine complex  $(\text{CH}_3\text{C}_6\text{H}_4\text{NO})\text{FePc}(\text{n-C}_4\text{H}_9\text{NH}_2)$  occurred by a dissociative reaction of  $\Delta H^\ddagger = 20.1 \text{ kcal mol}^{-1}$ . This is the only kinetic value for the enthalpy of activation of a dissociation reaction of a type I complex. DTA, DTG, and TG measurements have been made<sup>79</sup> on a NODMA complex of Pd<sup>II</sup>, the material being thermally stable up to about 200 °C.

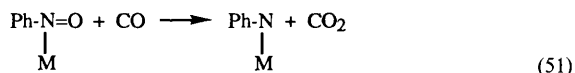
**D. Reduction and Deoxygenation Reactions.**—Ready reduction of the dinitrosoalkane ligand in cyclopentadienyl cobalt complexes is achieved by reaction with lithium aluminium hydride at  $-78$  to  $-50$  °C, the diamine being the product.<sup>62</sup> It appears that such reductions have not been attempted for most nitroso-compound complexes. There is, however, an unusual self-reduction reaction that has been reported for the nitrosobenzene tungsten pentacarbonyl complex which is stable in THF solution at  $-70$  °C and which on warming to 20 °C yields aniline tungsten pentacarbonyl.<sup>33</sup>

Deoxygenation of coordinated NOB occurs<sup>38</sup> when the type II complex  $\text{Ni}(\text{NOB})(\text{Bu}^t\text{NC})_2$  is boiled with *t*-butyl isocyanide in benzene, *t*-butylisocyanate being produced. Other electron donating agents which lead to N–O cleavage of the coordinated NOB with presumed phenyl nitrene formation are triphenylphosphine and nitrosobenzene. A further deoxygenation reaction by a tertiary phosphine to give a nitrene complex has been studied by La Monica and Cenini.<sup>49</sup>

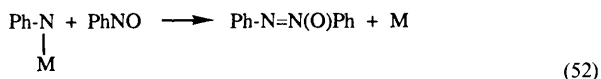


Unsuccessful attempts at deoxygenation of four complexes of 2-methyl-2-nitrosopropane using triphenylphosphine and *t*-butylisocyanide have recently been reported.<sup>16</sup>

Some type I nitrosoarene complexes of rhodium, iridium, ruthenium, palladium, and platinum react with carbon monoxide,<sup>34,35</sup> most probably by an initial oxygen abstraction giving a nitrene complex (equation 51).



In the presence of free nitrosobenzene further reaction occurs (reaction 52) giving azoxybenzene.



In ethanol, aniline is formed in equivalent quantities to the carbon dioxide presumably by a reaction of the coordinated nitrene with the protic solvent.

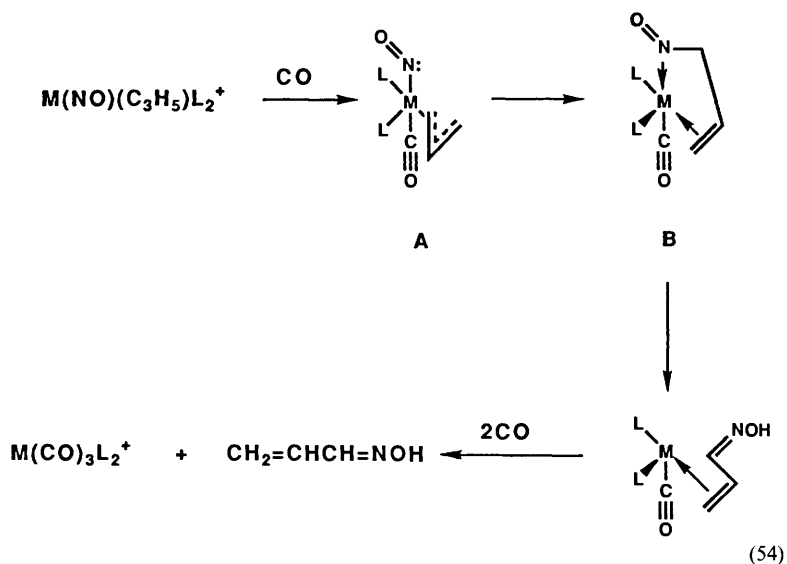
<sup>79</sup> D. N. Todor, A. Tanase, V. David, and G. E. Baiulescu, *Rev. Roum. Chem.*, 1989, **34**, 877.

These complexes may also be used to catalyse<sup>35a</sup> the conversion of nitrosobenzene and carbon monoxide into azoxybenzene and phenylisocyanate (benzene solution) and to urethane (ethanol solution). Similar complexes may be involved in the carbonylation of nitrosobenzene in the presence of palladium acetate and cupric acetate.<sup>35b</sup>

**E. Isomerization of Nitrosoalkane Ligands.**—The isomerization reaction of primary and secondary nitrosoalkanes to give the corresponding oxime has a long history with frequent, incorrect, attributions of the inability of the nitroso-compounds to be synthesized. The lack of kinetic investigations of reaction 53 makes it difficult to decide whether coordination of the nitroso-group to a



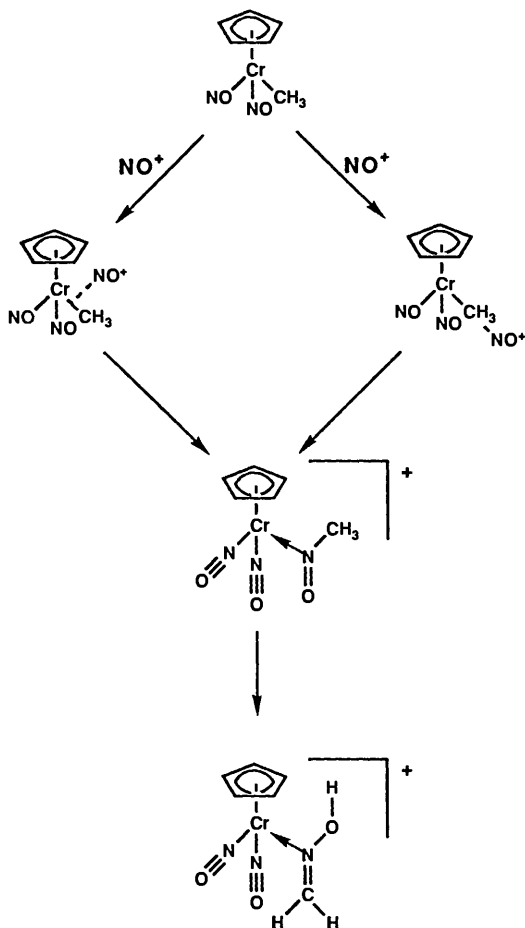
metal catalyses or inhibits the isomerization. The Legal complexes  $[Fe(CN)_5N(O)CH_2COR]^{3-}$  have lifetimes of only a few minutes<sup>52</sup> and presumably form oximes,  $RCOCH=NOH$ . A reaction sequence invoking a nitroso-propene intermediate has been proposed<sup>80</sup> for rhodium and iridium  $\eta^3$ -propene complexes (reaction 54).



A further proposal of an isomerization to oxime has been proposed<sup>67</sup> to account for the formation of a formaldoxime chromium complex *via* insertion of the nitrosonium ion into a chromium–methyl bond (Scheme 5).

<sup>80</sup> M. W. Schoonover, E. C. Baker, and R. Eisenberg, *J. Am. Chem. Soc.*, 1979, **101**, 1880.



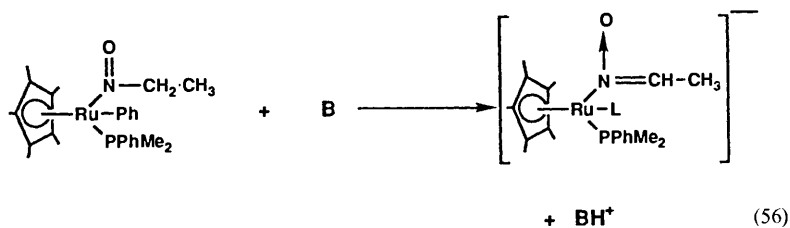
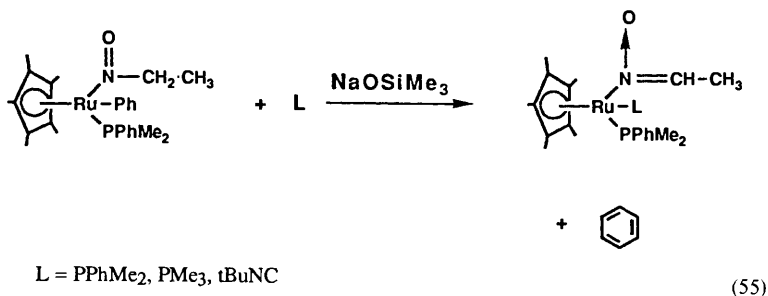


Scheme 5

Detailed investigation of nitroso  $\rightarrow$  oxime reactions in other nitrosoalkane complexes is required in order to understand the mechanism of these isomerizations.

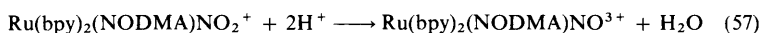
**F. Reaction with Bases.**—A systematic examination has been made<sup>66</sup> of the reactions of some nitrosoethane ruthenium compounds with bases in the presence of trisubstituted phosphines or *t*-butyl isocyanide. The overall reaction leads to an oximate complex (reaction 55).

From detailed kinetic studies the initial step is proposed to be as shown in reaction 56, *i.e.* a bimolecular step that is first order both in the complex and in the



Brönsted base. At present these results are unparalleled for other nitrosoalkane complexes.

**G. Reaction with Acids.**—An interesting protonation of type II coordinated NOB in  $\text{OsCl}(\text{NO})\text{NOB}(\text{PPh}_3)_2$  occurs<sup>40</sup> when this nucleophilic ligand of an osmium complex is interacted with aqueous hydrochloric acid. The protonated product is probably a divalent hydroxylaminato-osmium complex  $[\text{OsCl}_2\{\text{N}(\text{OH})(\text{Ph})\text{-(NO)}(\text{PPh}_3)_2\}]$ . Reaction of a nitro-group with acid in a type I NODMA complex has been reported.<sup>68</sup>



There are very few reports of reactions of complexes of nitroso-compounds with acids.

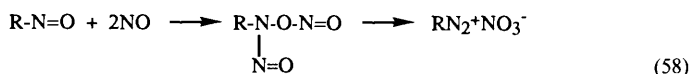
**H. Reaction with Oxygen.**—The majority of the complexes reported in the literature are stable to air. Some, however, can only be prepared with total exclusion of oxygen. The nickel(0) complexes  $(\text{RNO})\text{NiL}_2$  are examples. It is reported that the products obtained from bubbling oxygen through a benzene solution of one such complex ( $\text{R} = \text{Bu}^t$ ) are a precipitate (probably nickel hydroxide) and approximately equimolar quantities of 2-methyl-2-nitrosopropane and 2-methyl-2-nitropropane.<sup>44</sup> Another irreversible oxidation in benzene solution is found<sup>81</sup> for the  $\text{Fe}(\text{porphyrin})(\text{Pr}^t\text{NO})(\text{L})$  complexes, the stability of the complexes depending upon the magnitude of the binding constant of the ligand. It

<sup>81</sup> D. Mansuy, P. Battioni, J.-C. Chottard, C. Riche, and A. Chiaroni, *J. Am. Chem. Soc.*, 1983, **105**, 455.

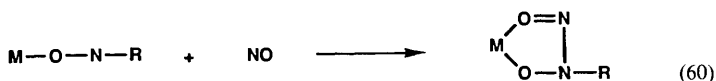
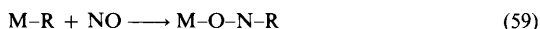
is therefore probable that the oxidation process is due to the interaction of oxygen with the pentacoordinate species  $\text{Fe}(\text{porphyrin})(\text{Pr}^i\text{NO})$ .

As an example of the resistance of many complexes to oxidation the failure to observe any reaction<sup>34</sup> for a number of rhodium and iridium type I complexes on boiling for twelve hours in aerated benzene is particularly noteworthy.

**I. Reactions with NO and  $\text{NO}^+$ .**—Uncoordinated nitroso-compounds can react with nitric oxide to form *N*-nitrosohydroxyl amine nitrites which rearrange to diazonium nitrates (58),

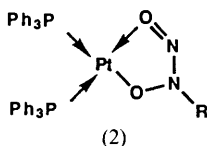


and it is of interest to investigate how the coordination mode of the nitroso-compound can modify this reactivity. The reaction of nitric oxide with some transition metal alkyls leads to the formation of *N*-alkyl-*N*-nitrosohydroxylamine compounds and reactions (59 and 60) have been proposed<sup>60</sup> to account for this invoking a paramagnetic nitrosoalkane intermediate.



It is, however, possible that the postulated intermediate is a type VII complex.

A similar reaction product results<sup>82</sup> when type II platinum complexes  $\text{Pt}(\text{RNO})(\text{PPh}_3)_2$  react with the nitrosyl cation to give the complex (2).

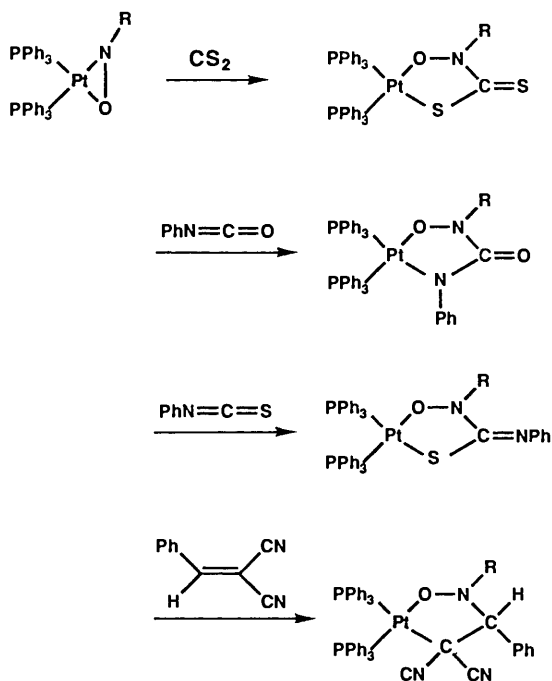


Reaction of the type II complex with nitric oxide, on the other hand, leads to the formation of a nitro-complex  $[\text{Pt}(\text{NO}_2)_2(\text{PPh}_3)_2]$ .

**J. Insertion Reactions into the Metal-Nitrogen Bond.**—An important class of reactions of type II platinum complexes  $\text{Pt}(\text{RNO})(\text{PPh}_3)_2$  is provided by insertion of another molecule into the metal-nitrogen bond. This class of reactions has been the subject of more sustained investigation than any other type of reaction of nitroso-compound complexes. The other reactant contains a double (or triple)

<sup>82</sup> C. J. Jones, J. A. McCleverty, and A. S. Rothin, *J. Chem. Soc., Dalton Trans.*, 1985, 401.

bonded function which can be incorporated into the Pt–N bond. The reactants carbon disulphide, phenyl isocyanate, phenyl isothiocyanate, and  $\beta,\beta$ -dicyanostyrene can insert into the Pt–N bond for the three cases R = Ph, Bu<sup>t</sup>, and CF<sub>3</sub><sup>39,83–86</sup> (Scheme 6).



Scheme 6

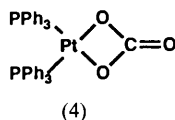
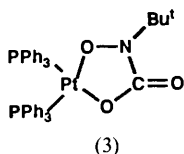
Other insertion reactions occur with tetracyanoethene (R = Ph,<sup>84</sup> CF<sub>3</sub><sup>39</sup>) and for dimethyl acetylenedicarboxylate (R = Ph,<sup>83</sup> Bu<sup>t</sup><sup>39</sup>). It is apparent that alkenes require substituent electron withdrawing CN groups for insertion to occur. Fumaronitrile undergoes insertion<sup>34</sup> (R = Ph) but this is also accompanied by displacement of the NOB to give the product (Ph<sub>3</sub>P)<sub>2</sub>Pt(NCCH=CHCN). The reaction with carbon dioxide shows the greatest differences between the different nitroso-ligands. When R = Ph insertion of carbon dioxide into the Pt–N bond takes place as for carbon disulphide,<sup>83</sup> but the CO<sub>2</sub> reaction is reversible.<sup>85</sup> When R = Bu<sup>t</sup> there are two products,<sup>39</sup> the insertion compound (3) and a carbonate complex (4); when R = CF<sub>3</sub> only the carbonate complex is formed.<sup>39</sup>

<sup>83</sup> P L Bellon, S Cenini, F Demartin, M Pizzotti, and F Porta, *J Chem Soc, Chem Commun*, 1982, 265

<sup>84</sup> S Cenini, F Porta, M Pizzotti, and G La Monica, *J Chem Soc, Dalton Trans*, 1984, 355

<sup>85</sup> S Cenini, F Porta, M Pizzotti, and C Crotti, *J Chem Soc, Dalton Trans*, 1985, 163

<sup>86</sup> F Demartin, M Pizzotti, F Porta, and S Cenini, *J Chem Soc, Dalton Trans*, 1987, 605



A further example of carbon dioxide insertion is provided by the rhodium complex<sup>87</sup> Rh(4-MeC<sub>6</sub>H<sub>4</sub>)[Bu<sup>t</sup>P(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]PhNO. Infrared evidence suggests that this is a type I complex and <sup>31</sup>P NMR implies that the insertion compound is present as two of the four possible stereoisomers in which the tolyl ligand can be coordinated either *cis* or *trans* to Rh-OC(O) or *syn* or *anti* with respect to the *t*-butyl substituent. We consider that it is more likely that the NOB complex dissociates to give a 16-electron Rh<sup>I</sup> species which then reacts with carbon dioxide and subsequently with NOB rather than that the carbon dioxide inserts into a type I Rh←N bond followed by subsequent rearrangement to produce a metallacyclic compound.

#### 4 Spectroscopy and Structure

The classification of coordinated nitroso-compounds into seven distinct classes<sup>16,17</sup> is a consequence of X-ray crystallographic studies and a sufficient number of studies has been made to establish the generality of these classes. The NO bond lengths that result show that in types II, III, IV, V, and VI the NO bond is much closer to the length characteristic of a single bond whereas in types I and VII the double bond character of the NO group is maintained.

X-Ray crystallographic studies are lacking for many coordination compounds and correlations have been attempted between infra-red spectroscopy and coordination mode. It has been suggested that as the NO stretching frequency is altered upon coordination, the change in frequency can be correlated with coordination mode. Coordination by types II and III leads to a large drop in  $\nu_{\text{NO}}$ , of about 400 cm<sup>-1</sup>, which is expected on the basis of the bond lengthening and  $\pi$  electron donation and in these cases the correlation is relatively straightforward. We have shown elsewhere<sup>17</sup> that there is a direct interdependence of  $\nu_{\text{NO}}$  with NO bond length in *C*-nitroso-compounds. Type I coordination usually leads to a slight extension of the NO bond and thus it is to be expected that  $\nu_{\text{NO}}$  will decrease by a small amount on coordination. The major problems arise for type VII coordination which is apparently confined to *p*-substituted nitrosoanilines such as NODMA coordinated to *d*<sup>9</sup> or *d*<sup>10</sup> metals. For some time incorrect attributions of  $\nu_{\text{NO}}$  in NODMA have been employed<sup>88</sup> and thus the correlation of type VII coordination with a small rise in  $\nu_{\text{NO}}$  is insecure. This is further emphasized by the fact that in the two examples of crystallographic study of type VII NODMA complexes the NO bond lengths are 1.218 Å<sup>24</sup> and 1.305 Å<sup>89</sup> and therefore it is to be expected that in the first of these the  $\nu_{\text{NO}}$  value will rise whereas in the second it will fall.

<sup>87</sup> L. Dahlenburg and C. Prengel, *Inorg. Chim. Acta*, 1986, **122**, 55.

<sup>88</sup> M. Cameron, B. G. Gowenlock, and G. Vasapollo, *J. Organomet. Chem.*, 1989, **378**, 493.

<sup>89</sup> S. Hu, D. M. Thompson, P. O. Ikekwere, R. J. Barton, K. E. Johnson, and B. E. Robertson, *Inorg. Chem.*, 1989, **28**, 4552

Other spectroscopic techniques have been used to confirm structures of coordinated nitroso-compounds. Frank and Bunbury<sup>90</sup> used Mössbauer spectroscopy to show that five nitroso-aromatic iron tricarbonyls had the same structure independent of the character of the substituents in the aromatic ring. Combination of this evidence with the X-ray crystallographic evidence<sup>91</sup> for one of the compounds emphasized the fact that type III coordination was operative in all cases and that the varying association character implied by molecular weight determinations<sup>4,8</sup> was not in evidence in the solid state which illustrated dimeric structure. Recently it has been shown<sup>92</sup> that the Mössbauer spectrum for triphenyl-phosphine nitrosobenzene iron dicarbonyl<sup>14</sup> has the same features that characterize the above tricarbonyls and that therefore this material is also dimeric in the solid state.

The use of X-ray photoelectron spectroscopy (XPS) in distinguishing between monomeric and dimeric C-nitroso-compounds<sup>93</sup> suggested to us that it could be applied to discriminating between the structural types of coordination compounds. In the case of uncoordinated nitroso-compounds it has been shown<sup>93</sup> that the difference between the O 1s peak and the N 1s peak  $\Delta E_B(\text{O-N})$  is about 133–134 eV for monomers and 128–129 eV for either *cis* or *trans* dimers. In coordination compounds of type I the value of  $\Delta E_B(\text{O-N})$  drops<sup>94</sup> by about 1.5–2.5 eV compared with that of the uncomplexed monomer, whereas there is no significant change in  $\Delta E_B(\text{O-N})$  for type II and type VII coordination. It seems likely that this technique could be further used to distinguish between type I and type VII coordination by NODMA.

NMR spectroscopy may be used as a structural tool for coordinated nitroso-compounds. In Table 1 the available <sup>1</sup>H and <sup>13</sup>C data for complexes of 2-methyl-2-nitrosopropane are presented. It should be noted that the C-NO value for the free monomer is at a higher frequency than for other t-butyl compounds thereby demonstrating the high electron withdrawing character of the –NO group. It is of particular interest therefore to note that type I coordination appears to increase this electron-withdrawing character. The preparation of further complexes of this ligand is obviously necessary in order to extend such generalizations and to relate them to the structure of the complexes. It may be noted that the *ipso*-C resonance in nitrosobenzene occurs at a higher frequency than for almost every other substituent, again demonstrating the high electron-withdrawing character of the –NO group and that in the coordination compound  $\text{K}^+(\text{NOB}\cdot\text{PtCl}_3)^-$  this resonance increases<sup>95</sup> by 6.2 ppm. Even when nitrosobenzene participates in type III coordination in  $(\text{NOB}\cdot\text{Fe}(\text{CO})_3)_2$  the resonance of the *ipso*-carbon<sup>96</sup> at

<sup>90</sup> E Frank and D St P Bunbury, *J Organomet Chem*, 1970, **23**, 229

<sup>91</sup> M J Barrow and O S Mills, *J Chem Soc A*, 1971, 864

<sup>92</sup> M Cameron, B G Gowenlock, and R V Parish, unpublished results

<sup>93</sup> C D Batch and D S Donald, *J Am Chem Soc*, 1984, **106**, 2758

<sup>94</sup> G Vasapollo, C F Nobile, A Sacco, B G Gowenlock, L Sabbatini, C Malatesta, and P Zamboni, *J Organomet Chem*, 1989, **378**, 239

<sup>95</sup> A S F Boyd, G Browne, B G Gowenlock, and P McKenna, *J Organomet Chem*, 1988, **345**, 217

<sup>96</sup> M Cameron and B G Gowenlock, unpublished results

<sup>97</sup> B M Al-Tahou and B G Gowenlock, *Rec Trav Chim*, 1986, **105**, 353

**Table 1** NMR data for Bu<sup>t</sup>NO and its coordination compounds (all values in ppm)

Compound	Me <sub>3</sub> C-NO	Me <sub>3</sub> C-NO	<sup>1</sup> H (δ)	Reference
Bu <sup>t</sup> NO	96.4	23.1	1.20	95,96
(Bu <sup>t</sup> NO) <sub>2</sub>	76.5	25.1	1.51	95,96
(Bu <sup>t</sup> NO) <sub>2</sub> PtCl <sub>2</sub>	105.6	27.4	1.80	95,32
(Bu <sup>t</sup> NOPtCl <sub>3</sub> ) <sup>-</sup> K <sup>+</sup>	105.4	27.5	1.70	95,32
Bu <sup>t</sup> NOW(CO) <sub>5</sub>	101	28.8	1.45	16,36
Bu <sup>t</sup> NOCpFe(CO)(PPh <sub>3</sub> )BF <sub>4</sub>	107.2	28.8	1.40	16
Bu <sup>t</sup> NOCpRu(PPh <sub>3</sub> ) <sub>2</sub> BF <sub>4</sub>	100.3	29.7	1.12	16
Bu <sup>t</sup> NOCpMn(CO) <sub>2</sub>			1.31/1.32	16,36

164.38 ppm is only slightly lower than in NOB itself,<sup>97</sup> suggesting that the electron-withdrawing characteristics of the -N=O group are retained despite the donation from both the N atom and from the π-NO bond.

The use of <sup>1</sup>H-NMR spectroscopy for structural correlations is best exemplified by the complexes of 2-methyl-2-nitrosopropane because all nine protons of the t-butyl group are equivalent. For the small number of type I complexes studied it is apparent that as *r*<sub>NO</sub> decreases both *v*<sub>NO</sub> and δ increase. The unusually low value of δ in the ruthenium compound suggests that a crystal structure value for *r*<sub>NO</sub> and N<sup>15</sup> labelling to pinpoint *v*<sub>NO</sub> would be important pieces of information necessary to sustain such correlations. The predicted, relatively long N=O bond (about 1.32–1.35 Å) could well lead to enhanced reactivity of the nitroso-ligand.

The theory of bonding in the most common, type I, complexes has received some attention following the earliest proposals<sup>68</sup> of metal ligand charge-transfer interactions leading to more detailed molecular orbital calculations.<sup>16,36</sup> The nitroso-ligand acts as a σ-donor *via* the overlap of the occupied HOMO, which is localized on the N atom with the metal *d*<sub>z<sup>2</sup></sub> orbital. In addition the nitroso-ligand acts as a π-acceptor, the occupied metal *d*<sub>xz</sub> orbital donating electron density into the unoccupied LUMO orbital π\* (*x*). The different degrees of π-donation from the metal to the ligand π\* orbital lead to the varying *v*<sub>NO</sub> values of the ligand. Weak π-π\* donation results in very little change in *v*<sub>NO</sub> and *r*<sub>NO</sub> from the values of the uncomplexed ligand as was first pointed out by Bowden<sup>68</sup> and by Mansuy.<sup>32</sup> It is important therefore to note that if *v*<sub>NO</sub> can be unambiguously identified in type I complexes information is provided on the extent of metal to ligand π-π\* donation. Further to this treatment the electronic spectra of the complexes can be understood in terms of a lowest energy electronic transition from the non-bonding *d*<sub>yz</sub>, *d*<sub>xy</sub> orbitals to the *d*<sub>xz</sub>-π\*(*x*) LUMO, a transition that has metal-to-nitroso charge-transfer character. Applications to the quantitative analysis of many transition metals are well established, see *e.g.* ref. 98. Studies of the photoelectron spectra of some type I tungsten and manganese complexes have also been reported<sup>36</sup> and it is of obvious importance for further studies to be attempted covering other types of complexes.

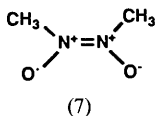
We have noted above that type VII complexes are confined to NODMA and

<sup>98</sup> R. B. Wilson and W. D. Jacobs, *Anal. Chem.*, 1961, **33**, 1652.

similar ligands in which there is a contribution from a dipolar quinonoid structure (5) to the monomeric nitrosoaniline (6).



X-Ray crystallographic investigations show that NODMA acts as a type I ligand to transition metals<sup>18,37</sup> and this is in contrast to its action as a type VII ligand to  $d^{10}$  metals such as tin<sup>24</sup> and zinc.<sup>89</sup> Type II coordination for NODMA has been reported for nickel<sup>38</sup> and for platinum<sup>94</sup> complexes. If type VII coordination is assisted by the partial negative charge on the oxygen in NODMA it is reasonable to assume that coordination by *cis*-dimeric nitrosomethane to tin<sup>76</sup> and lead<sup>75</sup> occurs similarly by the dimer molecule acting as a bidentate ligand bearing partial negative charges on both oxygen atoms (7).



Such a conclusion suggests the possibility of synthesizing other  $d^{10}$ -complexes containing *cis*-dimeric nitroso-compounds.

The most versatile nitroso-ligand is NOB, for which type I, II, III, IV, and V coordination is clearly established.

Although no theoretical studies of type II coordination have appeared, it seems probable that it is similar to  $\eta^2$ -alkene metal bonds in that there is  $\sigma$ -donation from the filled NO  $\pi$ -orbital into a vacant metal hybrid orbital accompanied by  $\pi$ -back-donation from a filled metal  $d$  orbital into the low lying vacant  $\pi^*$  NO orbital. The resultant lengthening of the NO bond to values in the range 1.41—1.45 Å shows that the bond is approaching single bond character and the hybridization of N changes up to  $sp^3$ . A further characteristic feature of  $\pi$  coordination by NOB is that the phenyl ring lies at an angle to the equatorial plane of the metal ON ring. In the three type III complexes whose structures have been determined the lengthening of the NO bond is slightly less (1.35—1.40 Å) whereas the hybridization change and twisting of the phenyl group from coplanarity with the NO bond is repeated.

In both of these types of  $\pi$ -bonded complexes there is a similarity to the alkene complexes of transition metals in the theoretical basis of bonding although the bond lengthening and lowering of vibrational frequency is much greater for NO than for CC. It has been noted that there are relatively few alkene complexes of the early transition metals and this is true for all types of C-nitroso-compound complexes of these metals. In Table 2 the existing position is displayed for nitroso-compound complexes of metals of groups 3—14 inclusive. In our opinion,



**Table 2** Metal complexes of C-nitroso-compounds arranged according to structural type and the periodic classification

3	4	5	6	7	8	9	10	11	12	13	14
Sc	Ti — <sup>a</sup> or <sup>h</sup>	V	Cr I <sup>a</sup> II <sup>d</sup>	Mn I <sup>a,c,d</sup>	Fe I <sup>a,c,d</sup> III <sup>a</sup> VI <sup>d</sup>	Co I <sup>b,e</sup> III <sup>a,d</sup>	Ni — <sup>b</sup> II <sup>a,b,c</sup>	Cu — <sup>b</sup> VII <sup>b</sup>	Zn VII <sup>b</sup> — <sup>h</sup>	Ga	Ge
Y	Zr	Nb II <sup>d</sup>	Mo I <sup>a</sup> II <sup>a,c,d</sup>	Tc	Ru I <sup>a,b,c,d</sup>	Rh I <sup>a,b</sup> III <sup>a</sup>	Pd I <sup>a,b</sup> II <sup>a</sup> III <sup>a</sup>	Ag	Cd — <sup>a</sup> or <sup>h</sup> VII <sup>b</sup>	In	Sn VII <sup>b</sup> — <sup>h</sup>
La — <sup>b</sup>	Hf	Ta	W I <sup>a,c</sup> II <sup>a</sup>	Re I <sup>a</sup> II <sup>d</sup> III <sup>d</sup> (?)	Os I <sup>f</sup> II <sup>a</sup>	Ir I <sup>a,b,g</sup>	Pt I <sup>a,c</sup> II <sup>a,b</sup> IV <sup>a</sup> V <sup>a</sup>	Au	Hg VII <sup>b</sup>	Tl	Pb — <sup>h</sup>

*a* = NOB or substituted NOB; *b* = NODMA or substituted NODMA; *c* = Bu'NO; *d* = other alkyl NO; *e* = dinitrosoalkane; *f* = HNO; *g* = nitrosoalkene; *h* = dimeric nitroso-compound. Coordinated type I—VII as in text. If type is unknown, indicated by —.

the coordination chemistry of nitroso-compounds, which is already both diverse and fascinating, is likely to develop rapidly.

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