

MOLECULAR NITROGEN AS A LIGAND

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ABSTRACT

The discovery and development of the chemistry of dinitrogen complexes are reviewed with particular reference to factors affecting their stabilities, and the implication of those factors in terms of electronic structure and energies is discussed.

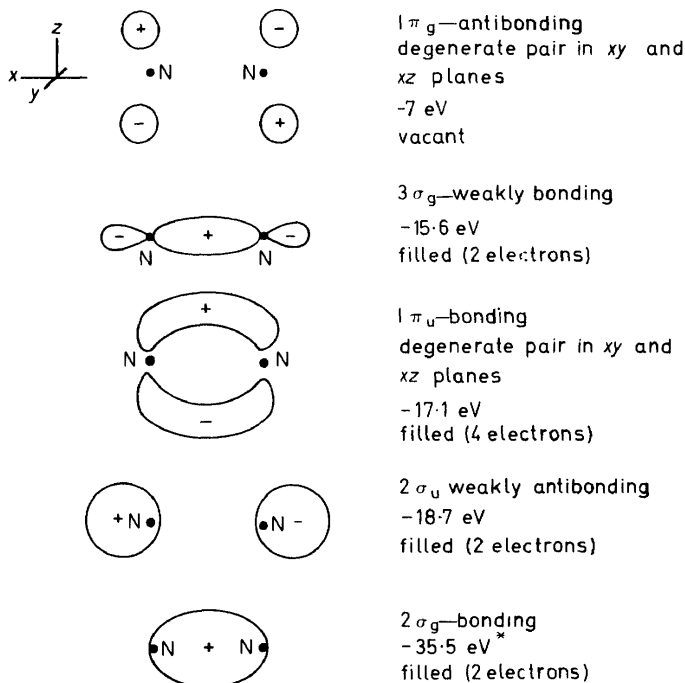
FIRST I must thank the organizers of this congress for their invitation to give a plenary lecture, and also I must explain my title. As you know, one is usually invited to give a plenary lecture some considerable time before the event, and to provide a title. But the subject changes continually and so I chose the somewhat vague title, 'Some reactions of nitrogen ligands', in the hope that I might be able to talk about the complex compounds containing molecular nitrogen as a ligand, but leaving the way open to talk about nitrido-complexes, or some other aspect of the complex chemistry of nitrogen should the complex chemistry of molecular nitrogen, i.e. dinitrogen, not come up to my expectations. However, I am pleased to say that development has been rapid and this lecture concerns only dinitrogen as a ligand. I have adjusted its title accordingly. I shall summarize briefly the pertinent properties of dinitrogen and of its complexes and discuss the factors which I believe are important in determining the bonding of dinitrogen in a transition metal complex.

The discovery of coordination compounds containing the nitrogen molecule as a ligand is one of the most exciting recent developments in the chemistry of nitrogen. Not that such compounds were unexpected; they had been so long in anticipation that most chemists had begun to believe that they could not exist. In 1930 Bortells¹ showed that traces of molybdenum were essential for the growth of nitrogen-fixing bacteria in the absence of any source of nitrogen other than dinitrogen, but in the presence of urea or ammonia the bacteria appeared to grow happily in the absence of molybdenum. Thus the molybdenum appeared to be directly involved with the nitrogen molecule in the process of fixation. This knowledge led to attempts to produce dinitrogen complexes by compressing the gas over molybdenum compounds but with no success. Similarly, a development of interest in olefin and acetylene complexes during the 1950s led to attempts to prepare dinitrogen analogues of the complex compounds of acetylene, but again of no avail. Most of these attempts went unpublished.

Indeed, all attempts to produce dinitrogen complexes were so negative that chemists became convinced that they would not exist as stable entities,

and the energy levels of the molecular orbitals in dinitrogen, as published by Mulliken² only ten years ago, provided sufficient reason. It was thus all the more surprising when they were eventually discovered, as was the very ease with which they were formed.

The electronic energy levels of dinitrogen differ from those found in any common analogous molecule, such as acetylene or dioxygen, in two important respects. First, the molecular orbital of highest energy is a σ -orbital and not a π -orbital. Secondly, the highest filled energy-level is of a very low energy indeed (-15.6 eV), whereas the highest vacant level is an antibonding π -level with a relatively high energy (-7 eV). The energy levels are set out schematically in *Figure 1*. The extremely low energy of the



* Estimated. Others are measured values.

Figure 1. Schematic representation of molecular-orbitals in dinitrogen with their energy levels

filled, and the high energy of the unfilled orbitals, explains the uniquely inert character of dinitrogen. Neither reduction nor oxidation of dinitrogen is easy, because it is difficult to remove electrons from the bonding orbital at -15.6 eV or, to put them into the lowest energy level, which is vacant, at -7 eV. The alkali metals, with ionization potentials of 3.4 to 3.9 eV, should be capable of doing the latter, but the placing of an electron in such strongly anti-bonding π^* -orbitals will weaken the molecule and alter all its energy levels. The N_2^- ion does not appear to be stable and dinitrogen can be reduced to nitride only when the metal forms a thermally very stable nitride, as does lithium. The early transition metals, e.g. titanium, also form very exo-

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thermic nitrides and are nitrided on the surface at room temperature by dinitrogen which is also reduced by titanium(II) compounds and compounds of similar metals in a very low oxidation state³. The unique character of the dinitrogen molecule in comparison with some similar molecules is evident from the physical properties listed in *Table 1* and they have been discussed at greater length in references 4 and 5.

Table 1. Some physical constants of dinitrogen and its analogues

	(HC) ₂	N ₂	O ₂	CO	NO
Bond length (Å)	1.208	1.098	1.207	1.128	1.150
Ionization potential (eV)	11.4	15.6	12.3	14.0	9.25
Dissociation energy (kcal)	199.6*	224.5	117.8	256.2	150.0
Stretching frequency (cm ⁻¹)	1974	2331	1555	2143	1876

* Bond energy

Ligand molecules are essentially electron donors, and dinitrogen is evidently a very poor donor. Its ionization potential of 15.58 eV is almost equal to that of argon (15.75), and much higher than that of acetylene (11.4) or even carbon monoxide (14.0). Thus at first sight dinitrogen seems to be about equal to argon in its ability to form coordination compounds. As an electron acceptor dinitrogen should also be poor with its lowest energy vacant orbital at -7 eV. However, as a concerted donor and acceptor, dinitrogen might attach itself to a transition metal with filled non-bonding *d*-orbitals in much the same manner as carbon monoxide. The bonding scheme is illustrated in *Figure 2* where the donor orbital is the 3σ_g-, and the

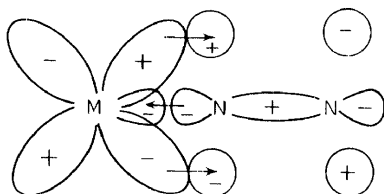


Figure 2. Schematic representation of a metal to nitrogen bond

acceptor orbitals are the 1π_g-molecular-orbitals. Such a bonding scheme requires an unusual arrangement of electronic energy levels in the metal atom. On the same metal atom one must have a σ-acceptor orbital of very low energy and π-type donor orbitals of very high energy. This seemed to be a somewhat impossible combination, and chemists were at last beginning to believe that dinitrogen complexes could not exist, when they were discovered.

DISCOVERY OF DINITROGEN COMPLEXES

In December 1965 Allen and Senoff⁶ announced the first recognized preparation of a dinitrogen complex. In samples of salts of [Ru(NH₃)₆]²⁺, prepared by the established method of treating an aqueous solution of ruthenium trichloride with hydrazine, they observed a strong, sharp band

between 2170 and 2115 cm^{-1} in the i.r. spectra. They were able to show that this band was caused by the $\text{N}\equiv\text{N}$ stretching vibration of a coordinated dinitrogen molecule in the ion $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$. Immediately afterwards Shilov, Shilova and Borod'ko⁷ reported the preparation of a related species prepared directly from dinitrogen by the reduction of ruthenium trichloride in anhydrous tetrahydrofuran with zinc amalgam, and they confirmed its nature by a preparation from $^{15}\text{N}_2$. They observed bands at 2140 cm^{-1} [$\nu(^{14}\text{N}\equiv^{14}\text{N})$] and 2070 cm^{-1} [$\nu(^{15}\text{N}\equiv^{15}\text{N})$] in their two products, and have recently shown that their product is converted to $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ by reaction with ammonia⁸.

Since 1965, by a combination of accident and feverish searching, dinitrogen has been introduced as a ligand into complex compounds directly from the gas phase⁷⁻¹⁹, from hydrazine and its organic derivatives^{6, 20-24}, from azide ion and its organic derivatives²⁵⁻²⁸, from ammonia²⁹, from nitrous oxide^{30, 31}, and by the reaction of nitrous acid with an ammine³². Nevertheless, few dinitrogen complexes are known. Most are mononuclear mono dinitrogen complexes, but three bis dinitrogen complexes^{22, 28, 32}, and three binuclear complexes with a bridging dinitrogen molecule^{13, 14, 33} have been reported. Many of the complexes are very unstable and only about a score of individual complexes have been completely characterized. The mononuclear complexes fall into three well-defined groups:

(1) Ammine and related complexes of osmium(II) and ruthenium(II) corresponding to the first known complex $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$.

(2) Tertiary phosphine complexes of the heavier transition metals, together with a halogen or a pseudohalogen and dinitrogen, e.g. $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ and $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$. There are also a few tertiary arsine complexes of the type $[\text{OsCl}_2(\text{N}_2)(\text{AsR}_3)_3]$.

(3) Tertiary phosphine complexes of the lighter Group VIII metals with dinitrogen and with or without hydrogen, e.g. $[\text{Co}(\text{N}_2)(\text{PPh}_3)_3]$ and $[\text{FeH}_2(\text{N}_2)(\text{PEt}_2\text{Ph})_3]$.

The known mononuclear compounds are summarized in *Tables 2, 3 and 4*.

Table 2. Ammine type dinitrogen complexes (other salts are known)

Complex	$\nu(\text{N}\equiv\text{N})^* \text{ cm}^{-1}$	Refs
$[\text{Ru}(\text{NH}_3)_5(\text{N}_2)] [\text{BF}_4]_2$	2144	6, 8, 10, 26, 29, 49, 57
<i>cis</i> - $[\text{Ru}(\text{N}_2)_2]_2 [\text{BPh}_4]_2$	2220, 2190	28
$[\text{Ru}(\text{N}_2)(\text{H}_2\text{O})] [\text{BPh}_4]_2$	2130	28
<i>cis</i> - $[\text{Ru}(\text{N}_3)\text{en}_2(\text{N}_2)] [\text{BPh}_4]$	—	28
$[\text{Os}(\text{NH}_3)_5(\text{N}_2)] [\text{BF}_4]_2$	2055, 2064 sh	21, 64
<i>cis</i> - $[\text{Os}(\text{NH}_3)_4(\text{N}_2)_2] \text{Cl}_2$	2120, 2175	32

* Solid state spectra

Ruthenium is the only element which shows some evidence of forming all three types. However, only the ammine and hydride types have been sufficiently characterized for inclusion in the tables. Most information concerning dinitrogen complexes is contained in preliminary communications and short notes and there has also been considerable changing of views concerning some of their compositions and reactions.

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 Table 3. Tertiary phosphine-halide type dinitrogen complexes
 (X = halogen or pseudohalogen; R = alkyl or aryl)

Complex	$\nu(\text{N}\equiv\text{N}) \text{ cm}^{-1}$	Refs
trans-[IrX(N ₂)(PR ₃) ₂]	2051–2113‡	25, 46, 50, 53, 58
[RhCl(N ₂)(PPh ₃) ₂]	2152	27
[OsX ₂ (N ₂)(PR ₃) ₃]	2062–2090†	17
[ReX(N ₂)L ₂ *]	1922–2035‡	24
[ReX(N ₂){Ph ₂ P(CH ₂) ₂ PPh ₂ } ₂]Cl	2035§	24

* L denotes ditertiary phosphine or two monotertiary phosphines.

† in benzene

‡ in CHCl₃

§ 'Nujol' mull

Table 4. Tertiary phosphine-hydride and metal(0) type of dinitrogen complexes

Complex	$\nu(\text{N}\equiv\text{N}) \text{ cm}^{-1}$	Refs
[Co(N ₂)(PPh ₃) ₃]	2088	} 9, 11, 34, 38, 39, 40, 41, 47, 59, 61, 62, 63, 65, 66
[CoH(N ₂)(PR ₃) ₃]	2033–2088	
[FeH ₂ (N ₂)(PR ₃) ₃]	2055–2060	15
[FeH ₂ (N ₂)(PEtPh ₂) ₂]	1989	15
[FeH(<i>o</i> -C ₆ H ₄ PEtPh)(N ₂)(PEtPh ₂) ₂]	—	15
[FeH(N ₂){Et ₂ P(CH ₂) ₂ PEt ₂ } ₂][BPh ₄]	2090	16
[RuH ₂ (N ₂)(PPh ₃) ₃]	2147	12, 18
[OsH ₂ (N ₂)(PEtPh ₂) ₃]	2082	36

All the dinitrogen complexes are derived from complexes of the transition metals in low, but positive, oxidation states. So far as is known, all are low-spin, and two with an odd number of electrons are paramagnetic^{24, 34}. There has been no substantiated report that dinitrogen in these complexes can be directly reduced to hydrazine or ammonia. The complexes behave generally as the inorganic analogues of the aliphatic diazo-compounds, in that most, but certainly not all, are highly reactive and they react to evolve molecular nitrogen.

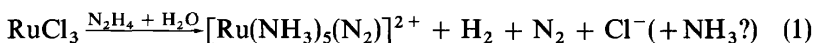
In general the stabilities of the dinitrogen complexes rise with increasing atomic number of the central metal atom in any Group and as one moves to the left across Group VIII into Group VIIA. However, the stabilities are very sensitive to the nature of the other ligands. These are usually tertiary phosphines and the change of one organic group in the phosphine for another, even methyl for phenyl, can be sufficient to destabilize the dinitrogen complex. Thus in a particular instance the triphenylphosphine dinitrogen complex may be prepared easily but its methyl-diphenylphosphine analogue may be unobtainable, or vice versa. Stability appears to depend on a critical balance of electronic energy levels in the metal atom and this leads to many individual exceptions to the general overall pattern of stabilities noted above.

PREPARATION OF DINITROGEN COMPLEXES

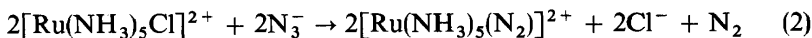
In the initial stages of the development of their chemistry, most dinitrogen complexes were discovered by accident and special preparative methods were found. Now a certain systematization is becoming evident.

Ammine type

(Ruthenium and osmium complexes, *Table 2*). These, exemplified by $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, may be obtained by the reaction of aqueous hydrazine with a halide of the metal (equation 1)^{21, 26}



This reaction works well in the preparation of $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, but the ruthenium analogue is contaminated with hydrazine, probably as $[\text{Ru}(\text{NH}_3)_5(\text{N}_2\text{H}_4)]^{2+}$, which is difficult to remove by recrystallization of its salts³⁵. It is preferable therefore to prepare these complexes by the reaction of the chloro-complex with azide ion^{26, 28} (equation 2).



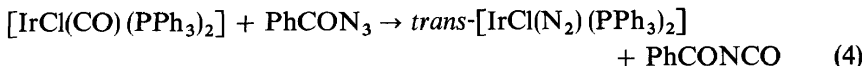
The intermediate pentaammine azide has a very limited stability. The mono-aqua ion $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ also reacts with azide ion to give the di-nitrogen complex³⁶. The di-aqua ion, *trans*- $[\text{Ru}(\text{H}_2\text{O})_2(\text{N}_2)]^{2+}$, with azide ion in aqueous solution at about 65° for 30 minutes, gives the azido-dinitrogen complex $[\text{Ru}(\text{N}_2)(\text{N}_3)]^{2+}$. This, by reaction with nitrous acid, yields the unstable bis-dinitrogen complex $[\text{Ru}(\text{N}_2)_2]^{2+}$ (ref. 28). A more stable bis-dinitrogen osmium complex has also been obtained by 'diazotization' of the ammine $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ (equation 3)³².



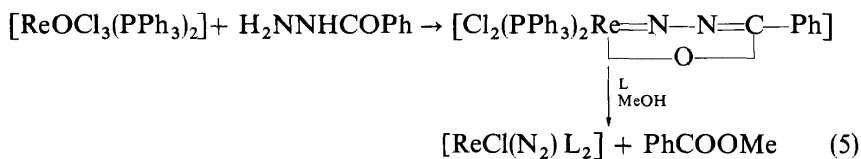
The aqua-complex $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ is a remarkable entity. It reacts directly with dinitrogen in aqueous solution to form the binuclear species $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{N}_2)]^{4+}$; this is the only known reaction of nitrogen gas in water at ordinary temperature and pressure¹³. It could well serve as a model for the uptake of dinitrogen by nitrogenase. The above ruthenium dimeric cation in aqueous solution is split by ammonia to form the salt $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, together with the $[\text{Ru}(\text{NH}_3)_6]^{2+}$ (ref. 13), or by dinitrogen at 100 atm to form $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ only³⁶.

Tertiary phosphine-halide types (*Table 3*)

Most of these have been obtained by splitting dinitrogen from an organic ligand. The first, $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$, was prepared by the reaction of an acid azide, e.g. benzoylazide, on the analogous carbonyl complex in reagent-grade chloroform, according to equation 4²⁵. This is a single example: corresponding carbonyl complexes containing other phosphines do not yield analogous dinitrogen complexes, although the very unstable rhodium analogue was prepared similarly³⁷.



A series of very stable rhenium(I) complexes, $[\text{ReCl}(\text{N}_2)\text{L}_2]$, where L is usually a ditertiary phosphine but may be two monophosphines, such as dimethylphenylphosphine, has been obtained by the reactions exemplified in equation 5²⁴.



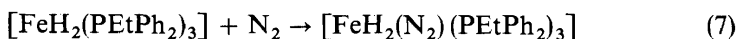
These dinitrogen complexes are particularly stable and some can be oxidized to give stable paramagnetic cations $[\text{ReCl}(\text{N}_2)\text{L}_2]^+$. The dinitrogen is so strongly held in $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_4]$ that in boiling toluene solution in the presence of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, the complex $[\text{ReCl}(\text{N}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]$ is formed without loss of dinitrogen²⁴.

The osmium(II) complexes $[\text{OsCl}_2(\text{N}_2)(\text{PR}_3)_3]$ were obtained directly by the reduction of the complexes $[\text{OsCl}_3(\text{PR}_3)_3]$ with amalgamated zinc in tetrahydrofuran under dinitrogen¹⁷. The reaction goes reasonably well at atmospheric pressure and very well at 100 atm. These complexes oxidize very readily in air in the presence of hydrochloric acid to revert to the trichloro-complex.

Tertiary phosphine-hydride and metal (0) types (Table 4)

These are considered together, e.g. $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$ and $[\text{Co}(\text{N}_2)(\text{PPh}_3)_3]$, because they are obtained by similar methods and, apart from reactions involving the hydride ligand, have a closely related chemistry. All are very sensitive to air and most have poor thermal stability.

The most general preparation is by the reaction of dinitrogen with a hydrido-tertiary phosphine complex of the metal (equations 6 and 7)^{11, 12, 15, 38, 39}.



These preparative reactions are often reversible and take place in protic solvents such as ethanol. The reaction of the cobalt hydride complex with dinitrogen provided the first evidence that dinitrogen was capable of reaction, under normal conditions of temperature and pressure, with a mild reagent such as could exist in a protic solvent.

These hydride or metal(0) types are also commonly obtained by the reduction of some complex of the metal using a strong reducing agent, such as an alkylaluminium, in the presence of an excess of the appropriate tertiary phosphine, and in a good stream of dinitrogen^{9, 40}. The products are often somewhat indeterminate. This certainly appears to be the case when cobalt(III) acetylacetonate is so treated. However, cobalt(II) acetylacetonate yields the pure non-hydridic complex³⁴, $[\text{Co}(\text{N}_2)(\text{PPh}_3)_3]$, and cobalt(III) acetylacetonate with dinitrogen containing dihydrogen, gives the hydridic complex $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$ as the only product⁴¹. Diisobutylaluminium hydride used as a reducing agent also tends to give the pure hydridic complex³⁶.

BINUCLEAR COMPLEXES

Dinitrogen can behave as a symmetrical bridging ligand. The best established example is $[(\text{NH}_3)_5\text{Ru}-\text{N}\equiv\text{N}-\text{Ru}(\text{NH}_3)_5]^{4+}$, obtained by the reaction of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ with dinitrogen, or with $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ (ref. 13). By the reaction of $[\text{Os}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ with the same aqua-complex, the mixed bridged complex $[(\text{NH}_3)_5\text{Os}-\text{N}\equiv\text{N}-\text{Ru}(\text{NH}_3)_5]^{4+}$ has been obtained³³, and a complex $[(\text{PCx}_3)_2\text{Ni}-\text{N}\equiv\text{N}-\text{Ni}(\text{PCx}_3)_2]$ (Cx = cyclohexyl) has also been reported¹⁴.

STRUCTURES

All completely characterized mononuclear dinitrogen complexes have strong bands assignable to $\nu(\text{N}\equiv\text{N})$ in the $1920-2175\text{ cm}^{-1}$ region of their i.r. spectra (Tables 2-4). This provides strong evidence that the dinitrogen molecule is bonded by one end to the metal as in Figure 2. The x-ray structure determination of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{Cl}_2$, although the structure is disordered, shows clearly that the ruthenium atom is octahedrally coordinated with a linear arrangement of the ruthenium and two nitrogen atoms of the dinitrogen ligand⁴². The structure of $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$ (Figure 3) shows a

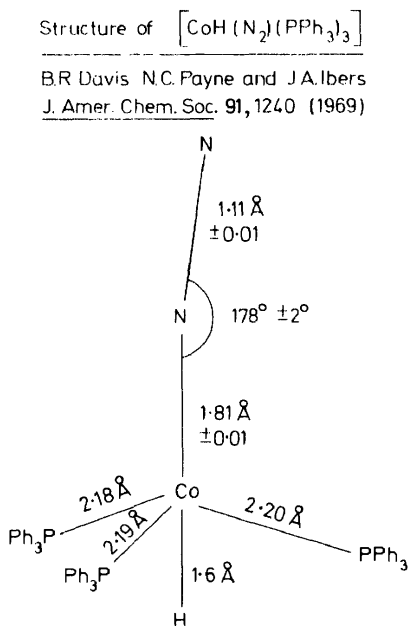


Figure 3. Structure of $[\text{CoH}(\text{N}_2)(\text{PPh}_3)_3]$

similar coordination of the dinitrogen⁴¹. Strong absorption in the i.r. spectrum assignable to $\nu(\text{N}\equiv\text{N})$ is the most useful diagnostic test for a dinitrogen complex; in solid state spectra this is often split into two or more bands, even in the spectra of pure mono-dinitrogen complexes³⁶.

There is still no real evidence that dinitrogen can attach itself symmetrically to a single metal atom, as acetylene does in its complexes. Under such

circumstances the dinitrogen stretching band in the i.r. spectrum of the complex would be very weak. There has been one report of such a complex, but this has not been confirmed in other laboratories⁴³.

The well-established binuclear ruthenium complex salt $[\{\text{Ru}(\text{NH}_3)_5\}_2(\text{N}_2)] [\text{BF}_4]_4$ shows no strong absorption assignable to $\nu(\text{N}\equiv\text{N})$ in its i.r. spectrum but it has a very strong band in its Raman spectrum at 2100 cm^{-1} , assigned to $\nu(\text{N}\equiv\text{N})$ by isotopic substitution with $^{15}\text{N}_2$ (ref. 44). The complex $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)] [\text{BF}_4]_2$ has $\nu(\text{N}\equiv\text{N})$ at 2133 cm^{-1} in the Raman spectrum. Thus the bond between the nitrogen atoms appears to be hardly affected by the addition of the second $\text{Ru}(\text{NH}_3)_5$ group. This is consistent with a linear $[(\text{NH}_3)_5\text{Ru}-\text{N}\equiv\text{N}-\text{Ru}(\text{NH}_3)_5]^{4+}$ type of structure, rather than a bent azo-type structure $[(\text{NH}_3)_5\text{Ru}-\text{N}=\text{N}-\text{Ru}(\text{NH}_3)_5]^{4+}$, which should show $\nu(\text{N}=\text{N})$ at a very much lower frequency.

REACTIONS

No reaction involving the rupture of the dinitrogen ligand or even the production of hydrazine has been found. Undoubtedly very strong reducing agents such as lithium metal in aprotic media would produce nitride, but such a reaction would not be interesting. It was once thought that the dinitrogen in $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ could be partly reduced to ammonia by sodium borohydride in water. This has been refuted³⁵. The reactions of dinitrogen complexes, in so far as they involve the dinitrogen moiety, are thus essentially displacement reactions. There are, however, interesting reactions not involving dinitrogen, but we need not consider them here.

The reversible replacement of dinitrogen by dihydrogen from some dinitrogen complexes is a very important reaction, because dihydrogen is a competitive inhibitor of nitrogen fixation in the biological process⁴⁵. This suggests that perhaps the enzyme nitrogenase may have a metal site which, so far as the uptake of dinitrogen is concerned, behaves in the same manner as the dinitrogen binding site in the tertiary phosphine-hydride or metal(0) type dinitrogen complexes.

Carbon monoxide is the closest analogue of dinitrogen in its complex chemistry and readily replaces dinitrogen irreversibly from most of its complexes. It is also a strong inhibitor of the natural fixation process⁴⁵. Unsaturated hydrocarbons also tend to displace the dinitrogen^{46, 47}, and acetylene, but not ethylene, is rapidly hydrogenated by nitrogenase⁴⁵. However, the rather strong, purely electron-donor type ligands, such as water and ammonia, do not compete effectively with dinitrogen, as in $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ mentioned earlier, which takes up dinitrogen from the very small concentration available in aqueous solution to displace the combined water, despite the enormous relative concentration of water. In the cobalt series of complexes dinitrogen and ammonia enter into reversible equilibrium⁴⁷ (equation 8).



Thus we see that the dinitrogen binding site is somewhat specific for so-called π -bonding ligands and hydride ion but scarcely binds the more common ligand molecules.

Attempts to protonate the dinitrogen in its complexes by hydrogen chloride have invariably led to the oxidation of the metal with elimination of dinitrogen, usually together with hydrogen, but never to the production of any ammonia or hydrazine⁴⁸, (e.g. equation 9). Direct oxidation of the complexes, e.g. $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ by ceric sulphate, also leads to quantitative liberation of dinitrogen¹⁰.



The dinitrogen complexes themselves are undoubtedly interesting, but no interesting reaction involving the dinitrogen ligand has been discovered. Their prime interest at present lies in the fact that they afford the only known reactions of dinitrogen which take place rapidly in protic media at ordinary temperature and pressure. The aqua-complex ion $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ reacts so readily with dinitrogen that it can compete effectively for the ruthenium site against dioxygen in ordinary atmospheric air and, since the oxidized ruthenium ion can be reduced, whereas the dinitrogen ruthenium complex cannot, it is possible by successive reductions and the passage of atmospheric air to convert the whole of the aqua-complex into the dinitrogen complex⁴⁹. In this respect the ruthenium complex proves more robust than nitrogenase, which after it has been rendered soluble in water is irreversibly destroyed by dioxygen⁴⁵.

THE NATURE OF THE DINITROGEN BONDING SITE

Chemists usually study the nature of the bonding to a new ligand by preparing a series of its complexes, and by varying the co-ligands in the complexes amongst ligands whose characters are already known. Thus they induce changes in the chemical and physical properties of the new ligand and so deduce something about its nature. Alternatively, they may replace the new ligand by other ligands whose nature is already known, and from the physical, particularly spectroscopic, properties of the substituting ligand deduce something about the bonding site of the unknown ligand. Both of these approaches have been proved useful in the case of dinitrogen complexes but the former is the less productive because stable series of dinitrogen complexes are almost unknown. Only a slight change in the co-ligands with dinitrogen is often sufficient to render the dinitrogen complex unstable. Thus dinitrogen appears to be very specific in its electronic requirements of the metal. This specificity is well illustrated in the series of iridium complexes, *trans*- $[\text{IrX}(\text{E})(\text{PR}_3)_2]$ (E = N₂ or CO). The carbonyl complexes can be prepared containing almost any mono-anionic ligand as the ligand X, and the organic groups may be alkyl or aryl. However, only three analogous dinitrogen complexes have been obtained pure. These are $[\text{IrX}(\text{N}_2)(\text{PPh}_3)_2]$ (X = Cl, Br or N₃)⁵⁰. Only an impure iodide can be obtained, because of instability. Attempts to prepare pure complexes containing other tertiary phosphines, even tri-*p*-tolylphosphine, have been unsuccessful. Similarly in other series it may be possible to prepare only one or two pure dinitrogen complexes but a whole series of carbonyl analogues. In the last few months reasonably extensive series of complexes have become available, namely $[\text{OsCl}_2(\text{N}_2)(\text{PR}_3)_3]$ ¹⁷ and $[\text{ReCl}(\text{N}_2)\text{L}_2]$ ²⁴ where L is a ditertiary phosphine

or two sterically small monotertiary phosphines but there has been no time to study these in detail.

The only general trend to emerge from the study of the relatively meagre series of dinitrogen complexes available, all containing aromatic tertiary phosphines, is that increasing alkyl substitution in the phosphine tends to decrease $\nu(\text{N}\equiv\text{N})$ (Table 5), and at the same time it often tends to destabilize the dinitrogen complex but there are exceptions and sometimes the steric factors may override the electronic.

Table 5. The effect of alkyl substitution in the tertiary phosphines on $\nu(\text{N}\equiv\text{N})$

PR_3	$[\text{IrCl}(\text{N}_2)(\text{PR}_3)_2]$	$[\text{OsCl}_2(\text{N}_2)(\text{PR}_3)_3]$	$[\text{CoH}(\text{N}_2)(\text{PR}_3)_3]$
PPh_3	2105 cm^{-1}	—	2096 cm^{-1}
PEtPh_2	2093	2090 cm^{-1}	2075
PEt_2Ph	2088	2063	2060
P(alk)_3		2069*	2060†

* PEt_3 † PBu_3

Evidence concerning the nature of the dinitrogen binding site has come mainly from comparative studies of corresponding dinitrogen carbonyl and organic cyanide complexes. The reactions of dinitrogen complexes show that nitrogen needs a site which holds π -bonding ligands, and is often capable of accommodating two hydride ions in place of dinitrogen but has little affinity for water or ammonia.

It is usually possible to obtain analogous dinitrogen and carbonyl complexes and their resemblances are much more striking than their differences. Structurally they are probably very similar. Thus the structure of the cobalt dinitrogen complex shown in Figure 3 might equally well have been the structure of a carbonyl complex. Moreover, substitution of alkyl for aryl groups, as mentioned in the previous paragraph, causes a decrease in $\nu(\text{C}\equiv\text{O})$ in the carbonyl complexes, just as it causes a decrease in $\nu(\text{N}\equiv\text{N})$ in the dinitrogen complexes. Also carbon monoxide and dinitrogen have essentially the same *trans*-influence as indicated by the closely similar $\nu(\text{M}-\text{Cl})$ and $\nu(\text{M}-\text{Br})$ in a few such compounds as *trans*- $[\text{IrX}(\text{E})(\text{PPh}_3)_2]$ ($\text{E} = \text{N}_2$ or CO , $\text{X} = \text{Cl}$ or Br) (Table 6)^{50,56}. It was noted early that in carbonyl analogues of dinitrogen complexes the carbonyl stretching frequencies are in the lower range of those found in terminal carbonyl

Table 6. Comparative *trans*-influence of N_2 and CO . [$\nu(\text{M}-\text{X})$ (cm^{-1}) in the grouping, $\text{E}-\text{M}-\text{X}$ ($\text{X} = \text{halogen}$)]

	$\text{E} = \text{N}_2$	$\text{E} = \text{CO}$	Refs
<i>trans</i> -complexes	$\nu(\text{M}-\text{X})$	$\nu(\text{M}-\text{X})$	
$[\text{IrCl}(\text{E})(\text{PPh}_3)_2]$	328	317	50
$[\text{IrBr}(\text{E})(\text{PPh}_3)_2]$	213	211	50
$[\text{RhCl}(\text{E})(\text{PPh}_3)_2]$	315	304	56

complexes. This indicates that dinitrogen needs a site where electrons in the non-bonding d -orbitals of the metal are high in energy and can drift strongly into the anti-bonding π -orbitals of the ligand. This is confirmed by a study of nitrile analogues of dinitrogen complexes in various laboratories^{36, 51, 52} and the figures in *Table 7* are ours. Normally in the nitrile complexes $\nu(\text{C}\equiv\text{N})$ is higher than in the free ligand but when nitriles take the place of dinitrogen $\nu(\text{C}\equiv\text{N})$ is usually lower than in the nitrile itself (*Table 7*), owing to electron drift into the antibonding $\text{C}\equiv\text{N}$ orbitals.

Table 7. $\nu(\text{C}\equiv\text{N})$ in nitrile analogues of $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]\text{X}_2$, (cm^{-1})

Nitrile	Ligand	DMSO	Cl	X		
				I	BF_4	PF_6
PhCN	2229	2178	—	2190	—	2219
<i>t</i> -BuCN	2235	2209	2212	2221	2229	2135
MeCN	2253	2229	2236	2239	2253	2276

Cf. $[\text{Co}(\text{NH}_3)_5(\text{NCMe})]^{3+}$ 2362; $[\text{Ru}(\text{NH}_3)_5(\text{NCMe})]^{2+}$ 2235 (in D_2O); MeCN— BF_3 2365; Pt(II)—MeCN complexes, 2280–2295 cm^{-1} .

The infra-red spectra give valuable information in the comparison of analogous series of dinitrogen and carbonyl complexes. Generally $\nu(\text{N}\equiv\text{N})$ and $\nu(\text{C}\equiv\text{O})$ rise and fall together but $\nu(\text{N}\equiv\text{N})$ is lowered very much more than $\nu(\text{C}\equiv\text{O})$ when the ligands enter a complex. This has been interpreted to suggest that there is a greater flow of electrons from the metal into the anti-bonding orbitals of dinitrogen than into those of carbon monoxide in their corresponding complexes⁵³, but if we compare the percentage lowering of frequency (P)* rather than the actual lowering, the lowerings in analogous

Table 8. Corresponding N_2 and CO stretching frequencies (ν) and their percentage lowering (P) ($E = \text{N}_2$ or CO)

E	$\nu(\text{N}\equiv\text{N})$	$P(\text{N}_2)$	$\nu(\text{C}\equiv\text{O})$	$P(\text{CO})$
E	2331 cm^{-1}	(0)	2140 cm^{-1}	(0)
$[\text{CoH}(\text{E})(\text{PPh}_3)_3]$	2088n	10.4	1910n	10.7
$[\text{IrCl}(\text{E})(\text{PPh}_3)_2]$	2104	9.7	1964	8.2
$[\text{IrBr}(\text{E})(\text{PPh}_3)_2]$	2108	9.6	1965	8.2
$[\text{OsCl}_2(\text{E})(\text{PMe}_2\text{Ph})_3]$	2082	10.7	1930	9.8
$[\text{OsBr}_2(\text{E})(\text{PMe}_2\text{Ph})_3]$	2092	10.3	1932	9.7
$[\text{ReCl}(\text{E})(\text{PMe}_2\text{Ph})_4]$	1922c	17.5	1780c	16.8
$[\text{Ru}(\text{NH}_3)_5(\text{E})]^{3+}$	2123w	8.9	1947w	9.0
$[\text{Ru}(\text{NH}_3)_5(\text{E})]^{2+}$	2093d	10.2	1922d	10.2

Spectra in benzene except n = 'Nujol' mull, c = CHCl_3 , w = H_2O , d = DMSO.

dinitrogen and carbonyl complexes are remarkably similar (*Table 8*). This, however, does not mean that the bonds holding carbon monoxide and dinitrogen to the metal atoms are almost identical. It is remarkable that the percentage lowerings are so nearly equal, because the orbitals involved in binding dinitrogen and in binding carbon monoxide to the metal are different.

* $P = \{100[\nu(\text{gas}) - \nu(\text{complex})]\} / \nu(\text{gas})$.

Those mainly involved in the dinitrogen molecule are the bonding $3\sigma_g$ -orbital, as a σ -electron donor, and the anti-bonding $1\pi_g$ -orbitals as d -electron acceptors (Figure 2). In carbon monoxide the corresponding orbitals are the formally non-bonding (actually weakly anti-bonding) sp -hybridized 5σ -orbital (at -14.0 eV) on carbon, and the anti-bonding 2π -orbitals (at ~ 6 eV), respectively^{54,55}. In the bonding of dinitrogen to the metal atom both electron donation by the nitrogen molecule and back donation by the metal should be $N\equiv N$ bond weakening, whereas in the bonding of carbon monoxide the electron donation should be very slightly $C\equiv O$ bond strengthening. Accordingly for similar electron drifts between the ligand and the metal one would expect *a priori* a greater percentage lowering of $\nu(N\equiv N)$ than of $\nu(C\equiv O)$. That the percentage lowerings are so closely similar suggests that the nitrogen is weaker in both its electron-donor function and its electron-acceptor function than is carbon monoxide in analogous complexes. Borod'ko and co-workers from similar data to ours reached the same conclusion⁵⁶ and a consistent conclusion was reached from a study of the Mössbauer spectra of the analogous pair of iron compounds *trans*- $[FeH(E)dpe_2][BPh_4]$ ($E = N_2$ or CO , $dpe = Et_2PCH_2CH_2PEt_2$)¹⁶.

Although dinitrogen requires a metal site where electron drift from the metal into the anti-bonding orbitals of the ligand is strong, peripheral structural changes in the complex which increase this drift, demonstrated by a lowering of $\nu(N\equiv N)$, do not necessarily increase the strength of bonding to dinitrogen. Indeed, they almost invariably destabilize the complex. Nevertheless, in an entirely different series of complexes one may find a very low $\nu(N\equiv N)$ accompanied by a very high stability. Thus the rhenium(I) series of complexes has high stability but some members have very low $\nu(N\equiv N)$ (Table 3) and even here aliphatic substitution on the phosphine causes destabilization³⁶. In my opinion this indicates that the metals generally have difficulty in satisfying the poor donor function of dinitrogen rather than its poor π -acceptor function, and any substitution which raises the energy of the σ -orbitals of the metal atom destabilizes the dinitrogen complex. Evidently in the known dinitrogen complexes the energy levels of these orbitals are usually on the upper limit for stability. Their energy can be lowered by oxidizing the metal atom, but this will also lower the energy level of the non-bonding d -orbitals, and then the acceptor function of the dinitrogen may not be satisfied. This latter doubtless accounts for the instability of such a hypothetical ion as $[Co(NH_3)_5(N_2)]^{3+}$ (ref. 67), which is isoelectronic with the well-known $[Ru(NH_3)_5(N_2)]^{2+}$. Thus, in my opinion dinitrogen complexes have so narrow a range of stability because the energy separation between the σ -bonding orbitals and the filled non-bonding d -orbitals on the metal must be so great that it can rarely be attained and at the same time satisfy both the donor and acceptor functions of the dinitrogen.

We can now see fairly clearly the type of site needed to bind dinitrogen and the factors which will help to produce it. I shall illustrate these with reference to octahedral complexes but the same principles will apply to any others. The molecular-orbital energy diagram for an octahedral complex (ignoring π -type bonding from metal to ligands) is shown in Figure 4. To obtain a reasonable bonding to dinitrogen the e_g-t_{2g} energy separation must

be large, to match the $3\sigma_g$ - and $1\pi^*$ -orbitals of the dinitrogen molecule sufficiently closely for good mixing; also the e_g level must be exceptionally low in energy because the $3\sigma_g$ level is exceptionally low. The e_g-t_{2g} energy separation is directly related to the $t_{2g}-e_g^*$ energy separation (Δ) in so far as ligand field splitting of the d -energy levels is a σ -effect. However, if the ligand has vacant orbitals (as has carbon monoxide) on an energy level such that good overlap with the t_{2g} -orbitals occurs, the t_{2g} -orbital energy will be

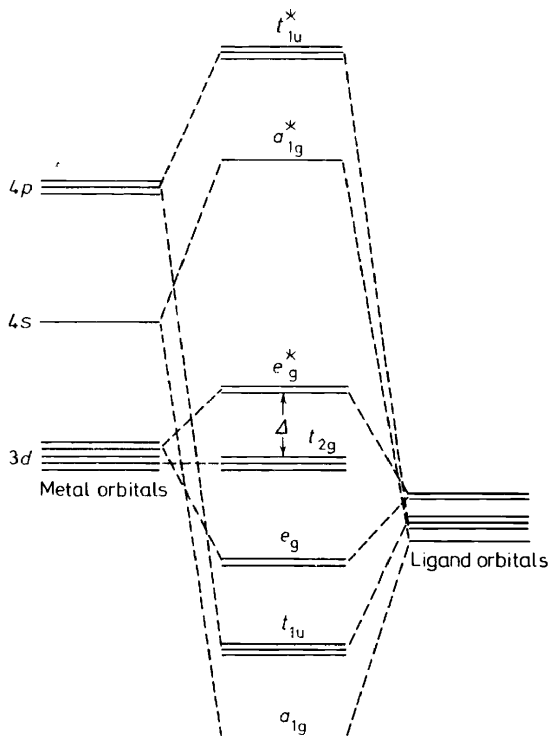


Figure 4. Molecular-orbital energy diagram for an octahedral complex ignoring π -type bonding from metal to ligands (* antibonding orbitals)

further lowered, and the increased Δ will be accompanied by a decrease in the e_g-t_{2g} energy separation. On the other hand, if the π -type orbitals on the ligand are filled and on an energy level similar to that of the t_{2g} -orbitals, then the t_{2g} -orbital energy will, in effect, be raised. Thus to get a large e_g-t_{2g} energy separation, as needed to stabilize dinitrogen complexes, one must choose ligands of high ligand field strength and without vacant orbitals of the correct symmetry and energy to combine to form π -type bonds with the t_{2g} -orbitals (e.g. H^- , CH_3^- and NH_3) or, if they have such orbitals, they must be so high in energy that the π -type bonding is weak (e.g. Ph^- , CN^- , PR_3 , AsR_3 and perhaps C_6H_6), or if they are of lower energy they must be filled (e.g. R_2O , H_2O).

The above-mentioned ligands are likely to be better than, say, olefins, CO, NO, R_2S , R_2Se , R_2Te , Cl^- , Br^- , I^- and perhaps C_5H_5 , all of which have

relatively low energy anti-bonding or *d*-orbitals which are vacant and capable of combining with the t_{2g} -orbitals of the metal, or like the halogens, of very low ligand field strength. The sulphide ligands are perhaps borderline in their ability to stabilize dinitrogen complexes.

Since occupied t_{2g} -orbitals on the metal atoms play an important part in the bonding to dinitrogen, transition metals in low oxidation states will generally form dinitrogen complexes. The e_g - t_{2g} separation is greater in the heavy transition elements than in the light elements in the same environment, and sufficient separation for the formation of stable dinitrogen complexes of the heavier elements might be attained with ligands of lower field strength. Thus it is possible, in the dinitrogen complexes of the heavier metals, to tolerate a few low strength ligands, such as chloride ion, in addition to high strength ligands, such as the tertiary phosphines. However, to the present, dinitrogen complexes of the first transition series of metals (Fe, Co and Ni), which contain an anionic ligand, use the high strength H^- ion rather than halide or similar ions. The above concept also explains why the heavier metals generally form the most stable dinitrogen complexes.

The matching of the energy levels of the e_g - and t_{2g} -orbitals with the $3\sigma_g$ - and $1\pi_g^*$ -orbitals of dinitrogen means that the metal is unlikely to form a dinitrogen complex in a negative oxidation state because the e_g -orbital would tend to have too high an energy for good overlap with the $1\pi_g^*$ -orbital. Thus it is unlikely that anions corresponding to the well-known $[Co(CO)_4]^-$ or $[Fe(CO)_4]^{2-}$ can be formed, as the latter can be formed from carbon monoxide, which has the corresponding σ -donor orbital at -14 eV. Also dinitrogen complexes of metals in high oxidation states, perhaps (III) or over, seem unlikely because the t_{2g} -orbitals will then be too low in energy to allow good back donation into the $1\pi_g^*$ -orbitals of the dinitrogen.

Thus the region of stability of dinitrogen complexes is very closely circumscribed by the necessity for a very high energy separation between the e_g - and t_{2g} -orbitals in octahedral complexes (or corresponding orbitals in others), and by the very small upward or downward adjustment in the energy levels of these orbitals which can take place before either the electron-donor or the electron-acceptor functions, respectively, of the dinitrogen, cease to be satisfied.

REFERENCES

- ¹ H. Bortells, *Arch. Mikrobiol.* **1**, 333 (1930).
- ² R. S. Mulliken, *Canad. J. Chem.* **36**, 10 (1958).
- ³ See M. E. Volpin, M. H. Ilatovskaya, L. V. Kosyakova and V. B. Shur, *Chem. Commun.* 1074 (1968);
G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Ed.* **7**, 386 (1968);
E. E. Van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley and B. Åkermark, *J. Amer. Chem. Soc.* **91**, 1551 (1969) and earlier references in all.
- ⁴ J. Chatt and G. J. Leigh, *Recent Aspects of Nitrogen Metabolism in Plants*, edited by E. J. Hewitt and C. V. Cutting, p 3. Academic Press: London and New York (1968).
- ⁵ J. Chatt, *Proc. Roy. Soc. B*, **172**, 327 (1969).
- ⁶ A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).
- ⁷ A. E. Shilov, A. K. Shilova and Yu. G. Borod'ko, *Kinetik i Kataliz*, **7**, 768 (1966).
- ⁸ Yu. G. Borod'ko, A. K. Shilova and A. E. Shilov, *Zh. Fiz. Khim.*, **44**, 627 (1970).
- ⁹ A. Yamamoto, S. Kitazume, L. S. Pu and S. Ikeda, *Chem. Commun.* 79 (1967).

- 10 D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.* **89**, 5706 (1967).
- 11 A. Sacco and M. Rossi, *Chem. Commun.* 316 (1967).
- 12 A. Yamamoto, S. Kitazume and S. Ikeda, *J. Amer. Chem. Soc.* **90**, 1089 (1968).
- 13 D. F. Harrison, E. Weissberger and H. Taube, *Science*, **159**, 320 (1968).
- 14 P. W. Jolly and K. Jonas, *Angew. Chem.* **80**, 705 (1968).
- 15 A. Sacco and M. Aresta, *Chem. Commun.* 1223 (1968).
- 16 G. M. Bancroft, M. J. Mays and B. E. Prater, *Chem. Commun.* 585 (1969).
- 17 J. Chatt, G. J. Leigh and R. L. Richards, *Chem. Commun.* 515 (1969).
- 18 W. H. Knoch, *J. Amer. Chem. Soc.* **90**, 7172 (1968).
- 19 M. Hidai, K. Tominari, Y. Uchida and A. Misono, *Chem. Commun.*, 814 (1969).
- 20 Yu. G. Borod'ko, V. S. Bukreev, G. J. Kozub, M. L. Khidekel and A. E. Shilov, *Zh. Strukt. Khim.* **8**, 542 (1967).
- 21 A. D. Allen and J. R. Stevens, *Chem. Commun.* 1147 (1967).
- 22 J. E. Fergusson and J. L. Love, *Chem. Commun.* 399 (1969).
- 23 J. Chatt, G. J. Leigh and D. M. P. Mingos, *Chem. & Ind.* 109 (1969).
- 24 J. Chatt, J. R. Dilworth and G. J. Leigh, *Chem. Commun.* 687 (1969).
- 25 J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.* **88**, 3459 (1966).
- 26 A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu and C. V. Senoff, *J. Amer. Chem. Soc.* **89**, 5595 (1967).
- 27 L. Yu. Ukhin, Yu. A. Shvetsov and M. L. Khidekel, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 957 (1967).
- 28 L. A. P. Kane-Maguire, P. F. Sheridan, F. Basolo and R. G. Pearson, *J. Amer. Chem. Soc.* **90**, 5295 (1968).
- 29 J. Chatt and J. E. Fergusson, *Chem. Commun.* 126 (1968).
- 30 L. Y. Sun, A. Yamamoto, and S. Ikeda, *Chem. Commun.* 189 (1969).
- 31 A. H. Diamantis and G. J. Sparrow, *Chem. Commun.* 469 (1969).
- 32 H. A. Scheidegger, J. N. Amor and H. Taube, *J. Amer. Chem. Soc.* **90**, 3263 (1968).
- 33 A. D. Allen and R. O. Harris, private communication concerning $[(\text{NH}_3)_5\text{Ru}-\text{N}\equiv\text{N}-\text{Os}(\text{NH}_3)_5]^{4+}$.
- 34 G. Speier and L. Markó, *Inorg. Chim. Acta*, **3**, 126 (1969).
- 35 J. Chatt, R. L. Richards, J. E. Fergusson and J. L. Love, *Chem. Commun.* 1522 (1968).
- 36 Unpublished observations from the author's laboratory.
- 37 L. Yu. Ukhin, Yu. A. Shvetsov and M. L. Khidekel, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 957 (1967).
- 38 A. Sacco and M. Rossi, *Inorg. Chim. Acta*, **2**, 127 (1968).
- 39 M. Rossi and A. Sacco, *Chem. Commun.* 471 (1969).
- 40 A. Misono, Y. Uchida and T. Saito, *Bull. Chem. Soc. Japan*, **40**, 700 (1967).
- 41 J. H. Enemark, B. R. Davis, J. A. McGinnety and J. A. Ibers, *Chem. Commun.* 96 (1968); B. R. Davis, N. C. Payne and J. A. Ibers, *J. Amer. Chem. Soc.* **91**, 1241 (1969).
- 42 F. Bottomley and S. C. Nyburg, *Acta Cryst., Camb.*, **B**, **23**, 1289 (1968).
- 43 G. J. Johnson and W. D. Beveridge, *Inorg. and Nuclear Chem. Lett.* **3**, 323 (1967).
- 44 J. Chatt, A. Nikolsky, R. L. Richards and R. J. Sanders, *Chem. Commun.* 154 (1969).
- 45 See review by R. W. F. Hardy and R. C. Burns, *Ann. Rev. Biochem.* **37**, 331 (1968).
- 46 J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.* **89**, 844 (1967).
- 47 A. Yamamoto, S. Kitazume, L. S. Pu and S. Ikeda, *J. Amer. Chem. Soc.* **89**, 3071 (1967).
- 48 J. Chatt, R. L. Richards, J. E. Fergusson and J. R. Sanders, *Nature, London*, **221**, 551 (1969).
- 49 A. D. Allen and F. Bottomley, *Canad. J. Chem.* **46**, 469 (1968).
- 50 J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc. (A)*, 2841 (1969).
- 51 P. C. Ford and R. E. Clarke, *Chem. Commun.* 1109 (1968); A. Misono, Y. Uchida, M. Hidai and T. Kuse, *Chem. Commun.* 208 (1969).
- 52 A. D. Allen, T. Eliades, R. O. Harris and P. Reinsalu, *Canad. J. Chem.* **47**, 1605 (1969).
- 53 J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun and J. W. Kang, *J. Amer. Chem. Soc.* **90**, 5430 (1968).
- 54 J. C. Slater, 'Quantum Theory of Molecules and Solids', Vol. I, pp 104 and 133. McGraw-Hill: New York (1963).
- 55 H. H. Jaffe and M. Orchin, *Tetrahedron*, **10**, 212 (1960).
- 56 U. G. Borod'ko, S. M. Vinogradova, U. P. Miagkov and D. D. Mozjukin, *Zh. Strukt. Khim.* **11**, 269 (1970).
- 57 I. J. Itzkovich and J. A. Page, *Canad. J. Chem.* **46**, 2743 (1968).

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- ⁵⁸ J. R. Collman, M. Kubota, J. Y. Sun and F. Vastine, *J. Amer. Chem. Soc.* **89**, 169 (1967).
- ⁵⁹ A. Misono, Y. Uchida, T. Saito and K. M. Song, *Chem. Commun.* 419 (1967).
- ⁶⁰ A. Yamamoto, S. Kitazume, L. S. Pu and S. Ikeda, *Proceedings of the Tenth International Conference on Coordination Chemistry*, Tokyo 1967, p 119;
A. Misono, Y. Uchida, T. Saito and K. M. Song, *Proceedings of the Tenth International Conference on Coordination Chemistry*, Tokyo 1967, p 122;
A. Sacco and M. Ross, *Proceedings of the Tenth International Conference on Coordination Chemistry*, Tokyo 1967, p 125.
- ⁶¹ G. W. Parshall, *J. Amer. Chem. Soc.* 1669 (1968).
- ⁶² A. Misono, Y. Uchida, M. Hidai and T. Kuse, *Chem. Commun.* 981 (1968).
- ⁶³ A. Misono, T. Uchida, M. Hidai and M. Araki, *Chem. Commun.* 1044 (1968).
- ⁶⁴ P. K. Das, J. M. Pratt, R. G. Smith, G. Swindon and W. J. U. Woolcock, *Chem. Commun.* 1539 (1968).
- ⁶⁵ A. Misono, Y. Uchida, T. Saito, M. Hidai and M. Araki, *Inorg. Chem.* **8**, 168 (1969).
- ⁶⁶ J. Lorberth, H. Noth and P. Rinze, *J. Organometallic Chem.* **16**, 1 (1969).
- ⁶⁷ R. B. Jordan, A. M. Sargeson and H. Taube, *Inorg. Chem.* **5**, 1091 (1966).