STUDIES ON THE REACTION OF MOLECULAR NITROGEN WITH SOME TRANSITION METAL COMPLEXES

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SUMMARY

The preparation of a nitrogen–iron system using molecular nitrogen is described. The complex $[Ru(NH_3)_5CO]I_2$ has been prepared and its relativity low $v(C\equiv O)$ at 1955 cm^{-1} is discussed.

INTRODUCTION

Within the last year it has become apparent that a variety of transition metal systems will react with molecular nitrogen forming metal–nitrogen complexes *e.g.* $HN_2Co(Ph_3P)_3$[1,2] and the ruthenium–nitrogen complexes[3,4]. In view of the occurence of iron in the nitrogen-fixing enzyme in biological systems, and the use of iron catalysts in the industrial fixation of nitrogen we have attempted to prepare iron–nitrogen complexes.

RESULTS AND DISCUSSION

Treatment of iron tris(acetylacetonate) in toluene or diethyl ether with triethylphosphine and triisobutylaluminium in a nitrogen atmosphere forms a dark blackish oil. Elemental analysis shows that the oil contains nitrogen ($\sim 2.3\%$), and the infrared spectrum shows a strong band at 2038 cm^{-1} which is in the region where the $v(N\equiv N)$ of other $M-N\equiv N$ systems is found. Careful and exacting efforts to obtain a pure compound from the oil were unsuccessful. In an attempt to obtain a purer product alternative routes were sought. It was found that treatment of the zero-valent complex, bis(cyclooctatetraene)iron with triethylphosphine under nitrogen gave a similar dark oil which also contained nitrogen and the same strong band at 2038 cm^{-1}. Also, addition of triethylphosphine to an ethereal solution of triallyliron gave a similar nitrogen containing product. Again a pure product was not obtained. On the basis of these results we conclude that the oily products contain a triethylphosphine–iron–nitrogen complex, possibly L_4FeN_2, $L=Et_3P$ and analogous to the recently reported ruthenium complex[5].

Attempts to prepare a rhodium–nitrogen complex using triallylrhodium and triethylphosphine in the presence of nitrogen were unsuccessful and complexes of the type π-allylbis(triethylphosphine)rhodium were obtained.

In order to gain insight into the nature of the $M-N\equiv N$ bond we prepared the carbonyl analogue of the nitrogen complex, $[Ru(NH_3)_5N_2]^{2+}$ by treatment of the

corresponding aquo complex with carbon monoxide. The carbonyl complex [Ru-(NH$_3$)$_5$CO]I$_2$ forms yellow, water soluble crystals. The infrared spectrum shows a strong band at 1955 cm^{-1} which may be assigned to the C≡O stretching frequency. It is interesting to observe that the carbonyl stretching frequency is rather lower than would be expected for a complex where the metal is formally in the +2 oxidation state. For example in neutral complexes of the type L$_2$Ru(CO)$_2$Cl$_2$, where L = Py, Dipy or Diphos, values for v(C≡O) in the region 2074–1985 cm^{-1} are reported[6]. It is well known that substitution of metal carbonyls with donor ligands such as amines causes a lowering of the v(C≡O) and this is attributed to the increase of electron density on the metal which gives rise in turn to a greater degree of back-donation from the metal to the π-anti-bonding carbonyl ligands. The relatively low position of v(C≡O) in the ruthenium complex suggests that the ammonia ligands are causing a relatively high electron density on the ruthenium which therefore increases back donation from the metal to the carbonyl group. We find that, in contrast to the nitrogen–ruthenium complex, the carbonyl complex at room temperature exchanges the carbonyl ligand for water either very slowly or not at all. The relative lability of the nitrogen ligand suggests it may be bonded less strongly than the carbon monoxide ligand.

The above data suggests that the (NH$_3$)$_5$Ru^{2+} system is capable of forming quite strong π-bonds with the carbonyl group. Slater LCAO-MO calculations[7] indicate that the $2p\sigma_g$ orbital of nitrogen is of lower (i.e. more negative) energy than the corresponding 5σ orbital of carbon monoxide by 1.7 eV but that the $2p\pi_g^*$ orbital of nitrogen is 0.3 eV higher than the anti-bonding 2π orbital of carbon monoxide. The difference in the σ-orbital energies of the two molecules suggests that the nitrogen should be an even weaker σ-donor than carbon monoxide, in agreement with chemical experience, and that the metal–nitrogen bond should therefore depend almost entirely on donation of electrons from the metal to the $2p\pi_g^*$ orbital of nitrogen. Since the nitrogen $2p\pi_g^*$ orbital is of higher energy than the corresponding orbital in carbon monoxide, it is to be expected that a metal will need to be in a slightly lower effective oxidation state to interact satisfactorily with nitrogen than it requires for bonding to carbon monoxide. Furthermore the $2p\pi_g^*$ orbital of nitrogen must overlap less effectively with metal orbitals than the anti-bonding 2π of carbon monoxide, since the latter has been calculated to be derived from 68% carbon $2p$ and 32% oxygen $2p$[7,8] and this is thus directed towards the metal. It is, however, reasonable to suppose that π-bonding in the metal–nitrogen bond is an important requirement for stabilisation of the M–N$_2$ system and that this will be most favoured when the metal is electron rich, i.e. has a relatively high electron density. This condition will often be associated with "low-oxidation state" complexes or when medium-oxidation state metals are bound by strongly donating ligands such as ammonia.

Many of the examples of systems which react with molecular nitrogen contain strong reducing agents, such as potassium metal or sodium naphthalenide. In such systems electron rich transition metal intermediates are likely to occur. Apart from electron-exchange reduction processes, electron-rich intermediates would also be produced by exchanging in a complex the π-acceptor and weakly donor ligands such as olefins with stronger donor ligands. This is the basis of the above reactions of Fe(0) olefin complexes with triethylphosphine. Triethylphosphine was chosen since it is believed to be a stronger donor than say aryl phosphines and yet has sufficient

π-acceptor character to stabilise low oxidation states. In other words a suitable ligand should not be so basic that the resulting complex would be unstable and dispro- portionate, e.g. $Fe(NH_3)_5$ would not be expected to be stable.

EXPERIMENTAL

Preparation of iron nitrogen complexes

(a) A mixture of iron (III) tris(acetylacetonate) (4.9 g), triethylphosphine (6.6 g), in toluene (40 ml) was treated with triisobutylaluminium (6.4 ml) at $-30°$ under nitrogen atmosphere. After an hour the reaction temperature was raised to 0–2° and nitrogen gas was passed through the mixture stirring, for about 24 h. The colour of the solution changed from dark brown to yellow and then to dark green. The solvent and volatile substances were removed in vacuum at room temperature and then $(30-40°)$ petroleum ether was added and the precipitate removed by filtration. Numerous attempts to crystallize out the complex from the filtrate or other solvents failed and chromatography of the petroleum ether solution of the products led to decomposition. The dark coloured viscous oil obtained by the removal of petroleum ether shows a strong band at $2038 \, cm^{-1}$ in the IR spectrum and the elemental analysis indicated the presence of nitrogen [2.3 %, calculated value for $(PEt_3)_4FeN_2$ is 5.0 %]. The possibility that this complex contains hydride ligand cannot be ruled out, although the attempts to detect hydride bands from the ^1H NMR spectrum failed due to paramagnetism of the sample.

(b) Triethylphosphine (1.8 g) was added to the suspension of bis(cycloocta- tetraene)iron (0.9 g)[9] in benzene (20 ml) through which a stream of nitrogen was passed at room temperature for 24 h. The solvent and other volatile substances were then removed in vacuum. The IR spectrum of the dark coloured viscous oil showed a strong band at $2038 \, cm^{-1}$ and the elemental analysis showed the presence of nitrogen (0.5 %).

(c) To the ether solution of triallyliron[10] was added triethylphosphine at $-70°$ and the reaction was carried out at 0–2° for 24 h under a nitrogen atmosphere. The ether was removed after the reaction and the dark-coloured viscous oil indicated the strong band in the IR spectrum at $2038 \, cm^{-1}$ and the elemental analysis showed the presence of nitrogen.

Carbonylpentaammineruthenium(II) iodide

A solution of $[Ru(NH_3)_5H_2O]^{2+}$ (0.07 mole) in 0.1 N H_2SO_4, prepared by reduction of the chloro-analogue with zinc amalgam, was treated with carbon monoxide for 48 h. The pH of the solution was adjusted to about 9 with dilute am- monia and treated with a stream of carbon monoxide for a further 24 h. The precipi- tate of $Zn(OH)_2$ was removed by filtration and a moderate excess of concentrated potassium iodide solution was added, giving a yellow precipitate. The precipitate was collected and recrystallised twice from warm water under a nitrogen atmosphere. The yellow crystals were dried *in vacuo* (30 %). (Found: C, 2.0; H, 3.23; N, 15.1. $CH_{15}I_2N_5ORu$ calcd.: C, 2.56; H, 3.23; N, 14.96 %.)

IR spectra

Spectra were determined on mulls in Nujol and hexachlorobutadiene using

a Perkin–Elmer 237 instrument. The data are: $[Ru(NH_3)_5CO]I_2$: 3225 vs, (b) (N–H str.), 2103 vw, 1955 s (C≡O str.), 1610 s (N–H def.), 1280 m, 775 s, 683 vw, 568 m.

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