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Nitrogen Fixation. II. Dinitrogen-Complexes of Iron

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The preparation and properties of dihydridodinitrogen complexes of iron(II), $FeH_2(N_2)L_3$ ($L = PetPh_2$, $PBuPh_2$, $PMePh_2$) are described. $FeH_2(N_2)(PEtPh_2)_3$ reacts with CO, to give the very stable $FeH_2(CO)(PEtPh_2)_3$. Both these complexes react in a 1:1 ratio with $AlEt_3$ and possible routes of reaction are discussed.

Introduction

Nitrogen complexes of iron(II), of formula $FeH_2(N_2)L_3$ ($L = PEtPh_2$, $PBuPh_2$) have previously been reported in a preliminary note.[1] In this paper we report the detailed preparation ,the properties and some reactions of the dinitrogen complexes.

Experimental Section

All the solvents were of reagent-grade quality and were dried, deaired and saturated with dry nitrogen. The reactions were carried out in an atmosphere of dry nitrogen, unless otherwise specified, by standard vacuum-line techniques.

Samples for m.p. determination were contained in evacuated tubes. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer and n.m.r. spectra on a Varian HA 100, using TMS as an internal reference.

Gaschromatographic determinations were carried out using a Carlo Erba Fractovap Mod. B.

Dihydridodinitrogentris(ethyldiphenylphosphine)iron (II). $FeH_2(N_2)(PEtPh_2)_3$.

(a) Ethyldiphenylphosphine (4,16 g, 19.4 mmols) was dissolved in 15 ml of ethanol and added to a solution of iron(II) chloride dihydrate (1.06 g, 6.3 mmols) in 25 ml of ethanol. To the slurry obtained after cooling to –10°C the reaction mixture, sodium borohydride (0.90 g, 23.8 mmols) dissolved in 25 ml of ethanol was slowly added under vigorous stirring. After the addition was complete (about 1 hour), stirring was continued at –10°C until the initial red precipitate became yellow-orange (about 5 hours).

After filtration at room temperature, the precipitate was washed with ethanol, water and lastly twice with ethanol, using about 5 ml of solvent each time. After drying in vacuo, the precipitate was extracted with benzene (3×5 ml), and the filtered benzene solution was partially evaporated in vacuo till a volume of about 5 ml. Light petroleum (20 ml) was added, and the mixture allowed to stand at room temperature for some hours. Yellow crystals precipitated, which were recrystallised from benzene (10 ml) by adding pentane (30 ml). Yield 3.2 g, 69.5%, d.p. 88°C.

Anal. Calcd for $C_{42}H_{47}N_2P_3Fe$: C, 69.22; H, 6.50; N, 3.85; P, 12.76; Fe, 7.66. Found: C, 69.60; H, 6.83; N, 3.88; P, 12.60; Fe, 7.62%.

(b) Tetrahydridotris(ethyldiphenylphosphine)iron[2] (0.40 g) suspended in light petroleum (20 ml) was kept for 1 hour under nitrogen and vigorous stirring. The seemingly unchanged crystals were filtered and dried in vacuo. The product was identified by means of its I.R. spectrum and analysis. Found: N, 3.84; P, 12.70; Fe, 7.70%.

Dihydridodinitrogentris(n-butyldiphenylphosphine)-iron (II). $FeH_2(N_2)(PBuPh_2)_3$. Tetrahydridotris(butyldiphenylphosphine)iron[2] (0.35 g) suspended in light petroleum (8 ml) was kept under nitrogen and vigorous stirring until the solid completely dissolved (about 30 minutes). Removal of the solvent in vacuo gave a yellow, creamy solid, very soluble in the organic solvents. Recrystallisation from a concentrated pentane solution at –30°C gave yellow crystals in poor yield. m.p. 39-41°C, d.p. 85-6°C.

Anal. Calcd for $C_{48}H_{59}N_2P_3Fe$:: N, 3.45; P, 11.43; Fe, 6.87. Found: N, 3.5; P, 11.5; Fe, 6.8%.

Dihydridocarbonyltris(ethyldiphenylphosphine)iron (II). $FeH_2(CO)(PEtPh_2)_3$.

(a) The corresponding dinitrogen complex (0.73 g, 1 mmol) was dissolved in benzene (15 ml) and the solution allowed to stand under carbon monoxide until the I.R. band at 2058 cm^{-1} completely disappeared. The solvent was the evaporated in vacuo and the yellow oily residue crystallised by adding ethanol. Recrystallisation from benzene plus ethanol gave the pure product in form of yellow crystals (0.70 g, 96%), d.p. 158°C.

Anal. Calcd for $C_{43}H_{47}OP_3Fe$: C, 70.9; H, 6.5; P, 12.75; Fe, 7.66. Found: C, 70.8; H, 6.4; P, 12.8; Fe, 7.6%.

(b) The compound, identified by means of its I.R. spectrum and d.p., was prepared in a similar manner from the corresponding tetrahydridocomplex and carbon monoxide.

Gaschromatographic determination of hydrogen, nitrogen and carbon monoxide. Samples of $FeH_2(N_2)$-

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(1) A. Sacco and M. Aresta *Chem. Comm.*, 1223 (1968).

(2) M. Aresta, P. Giannoccaro, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, *5*, 115 (1971).

Table I. Analytical Results

Compound	μmoles	Reagent	t, °C	N_2 μmoles	H_2 μmoles	CO μmoles	H_2/Fe	N_2/Fe	CO/Fe
$FeH_2(N_2)(PEtPh_2)_3$	30.3	Heat	150	29.6	12.9	—	0.42	0.98	—
»	38.7	I_2	50	38.6	38.5	—	1.0	1.0	—
»	45.8	HCl aq.	50	45.6	89.4	—	1.95	1.0	—
»	39.5	dp	110	39.1	—	—	—	0.99	—
$FeH_2(CO)(PEtPh_2)_3$	39.2	I_2	50	—	38.0	37.5	0.97	—	0.96

Table II. Infrared Absorption Bands (cm^{-1})

Compound	Solvent	νFe—H	νN_2	νCO	$\Delta\nu/\nu^{\circ}$ [b]
$FeH_2(N_2)(PEtPh_2)_3$	*a*	1960 vw, 1855 s	2055 vs		
»	C_6H_6	1840, w,l	2058 vs		0.117
$FeH_2(N_2)(PBuPh_2)_3$	*a*	1950 vw, 1863 s	2060 vs		
»	C_6H_6	1858 w,l	2065 vs		
$FeH_2(N_2)(PMePh_2)_3$	»	1881 w,l	2058 vs		
$FeH_2(CO)(PEtPh_2)_3$	*a*	1875 s		1900 vs	
»	C_6H_6	1870 sh		1900 vs	0.113
$FeH_2(N_2)(PEtPh_2)_3+AlEt_3$	»	1865 w,l	1989 vs		0.147
$FeH_2(CO)(PEtPh_2)_3+AlEt_3$	»			1870 vs	0.127

[a] Nujol mull. [b] $\Delta\nu=\nu^{\circ}_{N_2}-\nu_{N_2}$ or $\nu^{\circ}_{CO}-\nu_{CO}$; ν° = frequency in free ligand.

$(PEtPh_2)_3$ or $FeH_2(CO)(PEtPh_2)_3$ were treated, in current of argon, with an excess of iodine or hydrochloric acid in an apparatus connected to the gaschromatographic apparatus, as previously described.[3] The reaction with 1,2-bis(diphenylphosphino)ethane was carried out in boiling toluene, and the resulting dihydridodi{1,2–bis(diphenylphosphino)ethane}iron(II) was identified by means of its I.R. spectrum. Table I shows the results.

Reactions of $FeH_2(N_2)(PEtPh_2)_3$ and $FeH_2(CO)(PEtPh_2)_3$ with acceptor molecules. Samples of the complexes in anhydrous tetrahydrofuran or toluene solution were added to variable amounts of the following acceptor molecules, under an argon atmosphere: $ZnCl_2(THF)_2$, $MoCl_4(PEtPh_2)_2$, $MoCl_4(PEt_2Ph)_2$, $MoCl_4(PMePh_2)_2$, $AlEt_3$, BF_3.

The reactions were followed by recording the I.R. spectrum of the solutions. $ZnCl_2(THF)_2$ did not react. BF_3 and the molybdenum acceptor molecules at room temperature produced a rapid decomposition of the complexes; however, mixtures of the complexes with an excess of molybdenum acceptor molecules in toluene solution at –20°C were stable for several days, and did not show any shift of the dinitrogen or carbonyl absorption bands. On adding $AlEt_3$ to a toluene solution of the complexes, the I.R. spectrum showed a gradual disappearance of ν_{N_2} at 2058 cm^{-1} and ν_{CO} at 1900 cm^{-1}, beside the concomitant appearance of a strong absorption band at 1989 cm^{-1} for the dinitrogen complex, or at 1870 cm^{-1} for the carbonyl complex. The new bands at 1989 or 1870 cm^{-1} reached the maximum intensity, while the bands at 2058 or 1900 cm^{-1} completely disappeared, for a ratio $AlEt_3$/Fe = 1:1, and the I.R. spectrum did not show any further change by adding an excess of $AlEt_3$. On adding free phosphine, the original I.R. spectrum was restored.

Catalytic hydrogenation of propylene and 1-heptene. Mixtures of propylene and hydrogen, or 1-heptene and hydrogen were added at room temperature and under stirring to benzene solutions of $FeH_2(N_2)(PEtPh_2)_3$ (10^{-2} *M*) plus $AlEt_3$ (1.2×10^{-2} *M*). The systems gave rise to a slow absorption of hydrogen (about 10 ml/min), and the formation of propane, respectively heptane, was gaschromatographically detected in the reaction mixture (60-90% yield).

The same systems, but without $AlEt_3$, did not show any evidence of catalytic activity.

Results and Discussion

Dihydridodinitrogentris(ethyldiphenylphosphine)-iron (II) is a diamagnetic, pale yellow crystalline compound, fairly stable to air for some hours both in the solid state and in solution, soluble in non-polar solvents such as benzene, toluene, or tetrahydrofuran, insoluble in methanol, ethanol or petroleum ether. The corresponding complex with n-buthyldiphenylphosphine is very soluble in organic solvents and it is rather difficult to obtain the compound in a pure crystalline form. The corresponding complex with methyldiphenylphosphine has been detected only in solution.

The I.R. spectra of these complexes show, in the solid state, two absorption bands assignable to Fe-H stretching (Table II): one very weak at 1950-1960 cm^{-1}, and a stronger one at 1855-1863 cm^{-1}. Beside these bands the I.R. spectra show a very strong absorption band at 2055-2065 cm^{-1}, assignable to the N-N stretching of coordinated dinitrogen.

The n.m.r. spectrum in benzene, at room temperature, of the complex with ethyldiphenylphosphine shows a proton resonance quartet centered at 21.9 τ ($J_{P-H}=26$ cps). Owing to the stereochemical nonrigidity usually exhibited by six-coordinate iron hydrides,[4] the geometry of the molecule cannot be inferred until

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(3) A. Sacco and M. Rossi, *Inorg. Chim. Acta*, *2*, 127 (1968).

(4) P. Meakin *et al.*, *J. Am. Chem. Soc.*, *92*, 3482 (1970); E.L. Muetterties, *Acc. Chem. Res.*, *3*, 266 (1970).

Table III. Decomposition point, ν_{N_2}, and stability of some dinitrogen complexes

Compound	d.p.(°C)	ν_{N_2}(cm^{-1})	stability towards N_2 substitution	order of stability
class 1				
$[Ru(N_2)(NH_3)_5]X_2$ [a]	>100	2105-2167	fairly good	Os > Ru
$[Os(N_2)(NH_3)_5]X_2$ [b]	>200	2010-2060	good	
$RuCl_2(N_2)(PEt_2Ph)_3$ [c]		~2130	unstable	Os > Ru
$OsCl_2(N_2)(PEt_2Ph)_3$ [c]	130	2063	poor	
$RhCl(N_2)(PPh_3)_2$ [d]	<100	2152	very poor	Ir > Rh
$IrCl(N_2)(PPh_3)_2$ [e]	150	2105	poor	
class 2				
$CoH(N_2)(PPh_3)_3$ [f]	80	2090	poor	
$RhH(N_2)(PPh_3)_3$		unknown		Co > Rh,Ir
$IrH(N_2)(PPh_3)_3$		»		
$FeH_2(N_2)(PEtPh_2)_3$	88	2055	very good	
$RuH_2(N_2)(PPh_3)_3$ [g]	140	2147	poor	Fe > Ru > Os
$OsH_2(N_2)(PEtPh_2)_3$ [h]	20	2085	very poor	

[a] A.D. Allen et al., *J. Amer. Chem. Soc., 89,* 5595 (1967). [b] A.D. Allen and J.R. Stevens, *Chem. Comm.*, 1147 (1967). [c] J. Chatt et al., *J. Chem. Soc.* (A), 2243 (1970). [d] L. Yu. Ukhin et al., *Izv. Akad. Nauk. SSSR,* 957 (1967). [e] J.P. Collman et al., *J. Amer. Chem. Soc., 90,* 5430 (1968). [f] ref. 3. [g] ref. 5a. [h] ref. 6.

spectral temperature dependencies are examined.

The metal-dinitrogen bond in these iron-complexes is much more stable than that in the analogous cobalt-complexes[3] or in the corresponding ruthenium[5] and osmium complexes.[6]

The complex with ethyldiphenylphosphine does not react in solution with hydrogen, even under pressure, or with acetonitrile, pyridine, alkyl and aryl-amines, ammonia. Moreover, $FeH_4(PEtPh_2)_3$ is able to bound the atmospheric nitrogen in competition with oxygen, according to the equation:

$$FeH_4(PEtPh_2)_3 + N_2 = FeH_2(N_2)(PEtPh_2)_3 + H_2 \qquad (1)$$

On bubbling air in a toluene solution of the pure tetrahydrido-complex, the dihydridodinitrogen-complex is obtained in about a 20% yield. The same reaction, carried out in precence of an excess of free phosphine, gives the dihydridodinitrogen-complex in about a 50 per cent yield.

An atmospheric nitrogen fixation has previously been observed for a pentaammino ruthenium complex,[7] but only trough a rather complicated procedure, and the ruthenium system failed to fix, in only one step, the atmospheric nitrogen. Thus, $FeH_4(PEtPh_2)_3$ represents the first example of a simple and well characterized substrate able to fix directly the atmospheric nitrogen in succesful competition with the oxygen.

The dihydridodinitrogen complex reacts (see Table I) with iodine and with hydrochloric acid according to the equations:

$$FeH_2N_2(PEtPh_2)_3 + 4I_2 = FeI_2 + 3EtPh_2PI_2 + H_2 + N_2 \qquad (2)$$

$$FeH_2N_2(PEtPh_2)_3 + 2HCl = FeCl_2 + 3PEtPh_2 + 2H_2 + N_2 \qquad (3)$$

and with 1,2-bis(diphenylphosphino)ethane (dp) in boiling toluene according to the equation:

$$FeH_2(N_2)(PEtPh_2)_3 + 2dp = FeH_2(dp)_2 + 3PEtPh_2 + N_2 \qquad (4)$$

It is interesting to note that the order of relative stability of the metal-dinitrogen bond along the iron and cobalt triads (see Table III) depends on the absence (class 1) or the presence (class 2) of the hydride ligand in the complex. For analogous complexes of the class 1 the order of kinetic and thermodynamic stability is: 5d metals>4d metals, and the same trend is shown by the thermal stability and by the relative lowering of the stretching frequency of the coordinate dinitrogen. This order of stability is here in agreement with the order of increasing overlap of the molecular orbitals involved in the metal-dinitrogen bond, and, since a high electron density around the metal seems to be a fundamental requirement for the formation of the bond, it is not surprising that high-spin complexes, such as $FeCl_2(PR_3)_2$[8] and $CoCl(PR_3)_3$[9] are not able to bind the dinitrogen.

For the class 2 compound, the order of relative stability is: 3d metals>4d metals>5d metals, as suggested by the behaviour of the dinitrogen-complexes in reactions (5) and (6):

$$MH_2(N_2)P_3 + H_2 \rightleftharpoons MH_4P_3 + N_2 \qquad (5)$$

$$MH_2(N_2)P_3 + L \rightleftharpoons MH_2LP_3 + N_2 \qquad (6)$$

in which M = Fe, Ru, Os; P = tertiary phosphine; L = a neutral ligand, such as tertiary phosphine, pyridine, ammonia. The equilibrium of both reactions (5) and (6) is completely shifted to the left when M = Fe, completely shifted to the right when M = Os, and more or less shifted to the right when M = Ru.

The rhodium and iridium analogues of $CoH(N_2)(PPh_3)_3$ are unknown, but their instability can be inferred from the fact that neither $RhH(PPh_3)_3$,[10] unlike $CoH(PR_3)_3$,[11] nor $IrH_3(PPh_3)_3$,[12] unlike $CoH_3(PPh_3)_3$,[3] are able to react with the dinitrogen. However, here the order of stability is not related to the thermal stability, nor with the relative lowering of ν_{N_2}. The lack

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(5) (a) W.H. Knoth, *J. Am. Chem. Soc.*, *90*, 7122 (1968); (b) T. Jto, S. Kitazume, A. Yamamoto and S. Ikeda, *J. Am. Chem. Soc.*, *92*, 3011 (1970).

(6) B. Bell, J. Chatt, and G.J. Leigh, *Chem. Comm.*, 576 (1970).

(7) A.D. Allen and F. Bottomley, *Canad. J. Chem.*, *46*, 469 (1968).

(8) G. Booth and J. Chatt, *J. Chem. Soc.*, 2099 (1962).

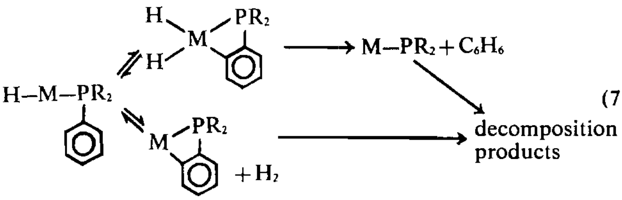
(9) M. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, *3*, 227 (1969).

(10) K.C. Dewhirst, W. Keim, and C.A. Reilly, *Inorg. Chem.*, 7 546 (1968).

(11) M. Rossi and A. Sacco, *Chem. Comm.*, 471 (1969).

(12) J. Chatt, R.S. Coffey, and B.L. Shaw, *J. Chem. Soc.*, 7391 (1965).

of correlation with the thermal stability can be understood if we consider that the decomposition of the hydridodinitrogen complexes does not correspond simply to the breaking of the metal-dinitrogen bond, but that for this class of compounds other concomitant reactions always occur, such as:


(7)

in which only the relevant ligands are shown. The breaking of the metal-dinitrogen bond can occur, both for steric and electronic factors, in different points of the reaction chain.

Both $FeH_4(PEtPh_2)_3$ and $FeH_2(N_2)(PEtPh_2)_3$ react under mild conditions with carbon monoxide, to give $FeH_2(CO)(PEtPt_2)_3$.

As usually found for analogous dinitrogen and carbonyl-complexes,[13] the relative lowering of the frequency of the ligands, $\Delta\nu/\nu^\circ$, (see Table II) are very similar.

$FeH_2(CO)(PEtPh_2)_3$ is a yellow crystalline compound, fairly stable to air, and it shows, as usually occurs for tertiary phosphine substituted hydridocarbonyl complexes, a much greater thermal and oxidative stability than the parent $FeH_2(CO)_4$. It is interesting to note, however, that $FeH_2(CO)_4$, in contrast to $RuH_2(CO)_4$ and $OsH_2(CO)_4$, undergoes hydrogen rather than carbonyl substitution, giving, by reaction with tertiary phosphine, d^8 five-coordinate derivatives, $Fe(CO)_4(PR_3)$ and $Fe(CO)_3(PR_3)_2$, instead of the expected d^6 six-coordinate derivatives.[14]

Both the dinitrogen and the carbonyl complexes with ethyldiphenylphosphine react with $AlEt_3$ in benzene solution in an 1:1 ratio: the stretching frequencies of the dinitrogen and carbonyl ligands are shifted respectively from 2058 cm^{-1} to 1989 cm^{-1}, and from 1900 cm^{-1} to 1870 cm^{-1}. All attempts to isolate the products of reaction were unsuccessful.

The observed decreasing of ν_{N_2} and ν_{CO} is compatible both with: (a) the formation of polynuclear bridged dinitrogen or carbonyl complexes, as previously suggested for a rhenium dinitrogen complex[15] and for a molybdenum carbonyl complex,[16] and with: (b) the removal of a phosphine ligand by the acceptor molecule, according to the equation:

$$FeH_2(L)(PR_3)_3 + AlEt_3 = FeH_2(L)(PR_3)_2 + R_3PAlEt_3 \qquad (8)$$

in which L is N_2 or CO.

However the following experimental data seem to support the latter hypothesis:

1) In contrast to the behaviour of the rhenium complex,[15] mixtures of the irondinitrogen complex and $ZnCl_2(THF)_2$ or $MoCl_4L_2$ (L = $PEtPh_2$, PEt_2Ph, $PMePh_2$) in tetrahydrofuran or xylene solution do not show any shift of ν_{N2} (see Table IV). All these acceptor molecules do not form, unlike $AlEt_3$ stable adducts with tertiary phosphines.

Table VI. $\Delta\nu_{N_2}$ of products from $FeH_2(N_2)(PEtPh_2)_3$ and $ReCl(N_2)(PMe_2Ph)_4$ with electron acceptor molecules.

Acceptor	$\Delta\nu_{N_2}(cm^{-1})$ Fe complex	Re complex
$AlEt_3$	69	32
$ZnCl_2(THF)_2$	0	42
$MoCl_4(PMePh_2)_2$	0	112
$MoCl_4(PEtPh_2)_2$	0	112

$\Delta\nu_{N_2} = \nu_{N_2}$ in starting complex—ν_{N_2} in adduct with acceptor.

2) $AlEt_3$ does not react, under the same conditions, with the analogous dinitrogen complex of cobalt, $CoH(N_2)(PPh_3)_3$.

3) In contrast to the behaviour of $FeH_2(N_2)(PEtPh_2)_3$ and $FeH_2(CO)(PEtPh_2)_3$, the 1:1 mixtures of these complexes with $AlEt_3$ are able to catalyze the hydrogenation of olefines. The catalytic activity could be related to the formation of an insatured d^6 pentacoordinate complex, as shown in the equation (8).

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(13) J. Chatt, D.P. Melville, and R.L. Richards, *J. Chem. Soc. (A)*, 2841 (1969).
(14) K. Farmery and M. Kilner, *J. Chem. Soc. (A)*, 634 (1970).
(15) J. Chatt *et al.*, *Chem. Comm.*, 955 (1970).
(16) J.C. Kotz and C.D. Turnipseed, *Chem. Comm.*, 41 (1970).