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SYNTHESIS AND REACTIONS OF AZIDO COMPLEXES OF IRON

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Abstract—Sodium azide reacts with $FeH_2(dmpe)_2$ (**1a**) [dmpe = 1,2-bis(dimethylphosphino) ethane] in methanol solution to form $FeH(N_3)(dmpe)_2$ (**3a**) and, finally, $Fe(N_3)_2(dmpe)_2$ (**2a**). The bis(azide) complex may also be generated from $FeCl_2(dmpe)_2$ (**4a**) by a ligand exchange reaction. The azide ligand is easily replaced by terminal alkynes to form bisacetylide iron complexes. The X-ray crystal structure of $Fe(N_3)_2(dmpe)_2$ (**2a**) shows that the azide groups are mutually *trans* and that the N—N—N groups are essentially linear and tilted by approximately 132° with respect to the plane containing the Fe and four P atoms.

Organic azides react photochemically with scission of the N—N_2 bond to form reactive nitrenes and thermally with alkenes and arenes to form heterocycles by a 1,3-dipolar addition.[1] In similar reactions, metal-coordinated azides are known to undergo dipolar additions with CS_2, nitriles and isonitriles to form coordinated heterocycles[2] and metal-bound azide has been employed in the synthesis of triazoles by [3+2] cycloadditions with acetylenes.[3]

Azide (N_3^-) is a good ligand and the azide group can be introduced relatively easily into transition metal complexes by substitution. Azide has been structurally characterized in metal complexes both as an η^1-ligand and as a bridging ligand with end-to-end coordination or with a terminal N of the N_3 group bridging two or more metal centres.[2a]

In the reaction of chelated cobalt azides with terminal acetylenes, the alkyne acts as an acid and protonation of bound azide with subsequent replacement of HN_3 by acetylide occurs to form cobalt acetylides.[3] Acetylide complexes of transition metals have been identified as potentially important precursors to materials with non-linear optical properties[4] and the investigation of alternative synthetic approaches to acetylide-bridged organometallic dimers, trimers and polymers is a developing area of organometallic chemistry. We have previously demonstrated[5] that metal bis(acetylide) complexes can be synthesized from $MH_2(PP)_2$ [M = Fe, Ru; PP = $R_2PCH_2CH_2PR_2$, R = Me, dmpe; Et, depe; Pr^n, dprpe] by reaction with terminal acetylenes in alcohol solution.

We report here the synthesis and properties of a series of stable iron azides and their reactions with terminal acetylenes to form iron acetylides.

RESULTS AND DISCUSSION

Synthesis and characterization of azido complexes

Iron dihydride complexes, $FeH_2(PP)_2$, provide precursors for a variety of metal complexes since,

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in methanol solution, the complexes are protonated to form $[FeH(H_2)(PP)_2]^+$ and the η^2-bound molecule of dihydrogen may be readily displaced by neutral ligands[6] (e.g. dinitrogen, nitriles and tertiary phosphines) or anions[7] (e.g. halides, thiolates and cyanide) under mild reaction conditions. When the phosphine ligand is dmpe, protonation is effectively quantitative in methanol[8] and displacement of the η^2-bound hydrogen by better ligands occurs rapidly at room temperature. Iron azides were formed readily by reaction of N_3^- with $[FeH(H_2)(dmpe)_2]^+$.

In a methanol solution of sodium azide, total conversion of $Fe(H)_2(dmpe)_2$ (**1a**) to $Fe(N_3)_2(dmpe)_2$ (**2a**) occurs through the intermediate azidohydrido complex, $Fe(H)(N_3)(dmpe)_2$ (**3a**), which is visible in the ^{31}P and ^1H NMR spectra at early stages in the reaction [$\delta_{P\{H\}}$(methanol-d_4) 71.5; δ_H(methanol-d_4) -22.75, quintet, $^2J_{PH} = 48.9$ Hz, Fe*H*] (Scheme 1).

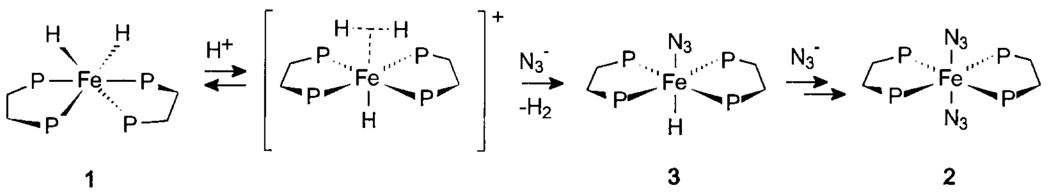
$Fe(H)_2(dmpe)_2$ (**1a**) is usually prepared by reduction of $FeCl_2(dmpe)_2$ (**4a**) as a very reactive and air-sensitive material.[9] $Fe(N_3)_2(dmpe)_2$ (**2a**) may also be prepared directly from $FeCl_2(dmpe)_2$ (**4a**) by displacement of the halide. Sodium azide reacts with $FeCl_2(dmpe)_2$ (**4a**) in a methanol solution to give initially the azido chloro complex, $Fe(N_3)Cl(dmpe)_2$ (**5a**), which has been isolated and characterized spectroscopically, and eventually $Fe(N_3)_2(dmpe)_2$ (**2a**) (Scheme 2). The bisazido iron complexes, $Fe(N_3)_2(depe)_2$ (**2b**) and $Fe(N_3)_2(dprpe)_2$ (**2c**) have been formed in an analogous manner to (**2a**) from the corresponding dichloro complexes $FeCl_2(depe)_2$[10] (**4b**) and $FeCl_2(dprpe)_2$ (**4c**).[11]

The azido complexes synthesized show one singlet resonance in the ^{31}P NMR spectrum, indicative of a *trans* complex in which the four phosphorus atoms of the chelating ligands are equivalent and occupy an equatorial plane around the metal atom.

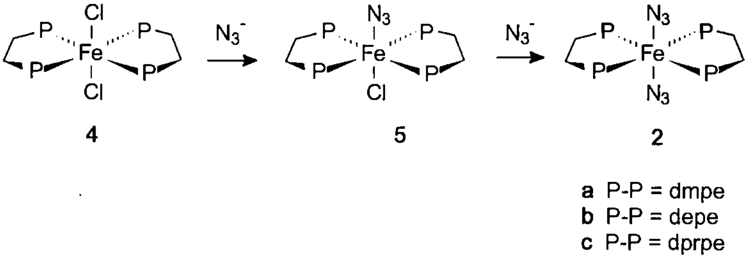
The ^1H NMR spectra of the azido complexes reflect the symmetry of the ligand environment, a more complex spectrum is observed in case of the azido chloro (**5a**) complex than in symmetrically substituted bisazido complexes (**2a–c**). The α methylene hydrogen atoms of the ethyl groups of depe and the propyl groups of dprpe are diastereotopic and give rise to complex multiplet patterns in the ^1H NMR spectrum on complexation with a metal. The metal-bound hydride ligand in $Fe(H)(N_3)(dmpe)_2$ (**3a**) is very shielded ($\delta - 22.75$) and the signal appears as a quintet ($^2J_{PH} = 48.9$ Hz), which collapses to a singlet resonance on ^{31}P decoupling.

The coordinated azido ligands are replaced by acetylide in an alcohol solvent. Bis(acetylide) complexes of iron, $Fe(C{\equiv}CR)_2(dmpe)_2$ (R = Ph, 4-$HC{\equiv}CC_6H_4$, Bu^t), are prepared in excellent yields from $Fe(N_3)_2(dmpe)_2$ (**2a**) by stirring a methanol solution of the complex with an excess of the appropriate terminal acetylene in the presence of sodium methoxide. This is a useful synthetic sequence since the direct reaction of acetylides with $FeCl_2(dmpe)_2$ (**4a**) typically results in the precipitation of the acetylide chloride complexes, $FeCl(C{\equiv}CR)(dmpe)_2$, which are poorly soluble in most protic solvents and relatively inert to further substitution.[11]

Reaction of azide with $FeCl(C{\equiv}CPh)(dmpe)_2$[12] forms the acetylide azido complex, $Fe(C{\equiv}CPh)(N_3)(dmpe)_2$ (**6a**). Although the reaction of



Scheme 1.



Scheme 2.

this acetylide azido complex with a terminal acetylene other than phenylacetylene potentially provides a method for the stepwise assembly of bis(acetylide) complexes incorporating different acetylide ligands, the phenylacetylide ligand in **6a** is itself labile and both the —C≡CPh and $—N_3$ groups are readily displaced on addition of a terminal acetylene.

The iron bisazido complexes are an intense blue colour, showing absorptions at approximately 580 and 670 nm in the visible spectrum. The azido hydride complex is yellow, similar in colour to $Fe(H)_2(dmpe)_2$ and the azido chloride complexes are light blue. Compared with the IR stretching frequency of free azide, the stretching frequency of the N_3 group is shifted approximately 12 cm^{-1} to lower energy on binding to the metal.

X-ray crystal structure of complex **2a**

The crystal structure of $Fe(N_3)_2(dmpe)_2$ (**2a**) (Fig. 1) shows the three nitrogen atoms of each azide group to be approximately linear and forming an angle of 132.3° with the equatorial plane containing the Fe atom and four P atoms (Table 1). This compares with an angle of 121.8° for $Fe—N—N_2$ in the complex $[Fe(N_3)(TPP)]$[13] (TPP = tetraphenylporphyrin), 116.7° for $Ru—N—N_2$ in the complex $[Ru(N_2)(N_3)(en)_2]^+$,[14] 132.9° in the complex $Ru(N_3)_2(depe)_2$,[15] 125.4° for $Cu—N—N_2$ in the complex $[Cu(Br)(N_3)(Et_2NCH_2CH_2N(H)CH_2CH_2NEt_2)_2]$,[16] and angles of between 121° and 129° for $Mo—N—N_2$ in the complex $[Mo(N_3)_4(NO)(H_2NO)]$.[17] The N—N bond lengths are 1.179 and 1.162 Å for FeN—N and NN—N, respectively, which compare with 1.186 and 1.192 Å for the corresponding bond lengths in $[Fe(N_3)(TPP)]$,[13] 1.179 and 1.146 Å for RuN—N and NN—N in the ruthenium complex $[Ru(N_2)(N_3)(en)_2]^+$,[14] and 1.180 and 1.170 Å for RuN—N and NN—N in $Ru(N_3)_2(depe)_2$.[15] The N—N bond lengths in HN_3 are 1.240 and 1.134 Å[18] and in N_3^- are 1.154 Å.[19] The azide groups in **2a** are positioned *anti* with respect to one another in the crystal.

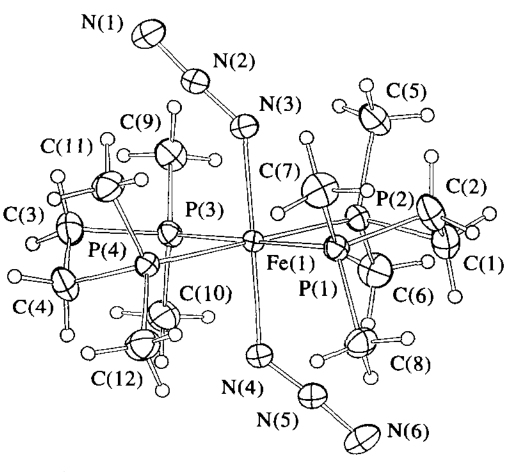


Fig. 1. View of the complex *trans*-$Fe(N_3)_2(dmpe)_2$ (**2a**) showing atom labelling.

Table 1. Selected bond lengths (Å) and angles (°) in *trans*-$Fe(N_3)_2(dmpe)_2$ (**2a**)

P(1)—Fe	2.239(1)	P(2)—Fe	2.237(1)
P(3)—Fe	2.242(1)	P(4)—Fe	2.242(1)
N(3)—Fe	2.024(3)	N(3)—N(2)	1.179(5)
N(2)—N(1)	1.162(5)	P(3)—C(3)	1.838(4)
C(3)—C(4)	1.509(5)	P(4)—C(4)	1.834(4)
P(3)—C(9)	1.824(4)	P(3)—C(10)	1.822(4)
P(1)—Fe—P(2)	85.6(0)	P(1)—Fe—P(3)	179.8(0)
P(1)—Fe—P(4)	94.5(0)	P(2)—Fe—P(3)	94.5(0)
P(1)—Fe—N(1)	91.2(1)	N(2)—N(3)—Fe	132.3(3)
Fe—P(3)—C(3)	108.3(1)	P(3)—C(3)—C(4)	107.8(3)

EXPERIMENTAL

General data

Tetrahydrofuran (THF) was distilled from benzophenone ketyl under nitrogen prior to use. Methanol was dried by distillation from magnesium methoxide.[20] Deuterated solvents were obtained from Merck and Aldrich and used as received. ^1H (400.1 MHz), ^{31}P (162.0 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded on a Bruker AMX-400 spectrometer, in the solvents indicated. ^{31}P NMR spectra were referenced to neat external $P(OMe)_3$ taken as $\delta 140.85$, ^1H and ^{13}C NMR spectra were referenced to solvent residuals. UV–vis spectra were recorded on a Hitachi 150-20 spectrophotometer with THF as the solvent. IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer with the sample in a Nujol mull. Electron impact mass spectra were obtained using an AEI-MS30 mass spectrometer. Microanalyses were performed by the University of New South Wales Analytical Chemistry Laboratories and the National Analytical Laboratories. Nitrogen (>99.5%) was obtained from Commonwealth Industrial Gases (C.I.G.) and used as received. Phenylacetylene and tert-butylacetylene were obtained from Aldrich and distilled before use. $FeH_2(dmpe)_2$ (**1a**),[9] $FeCl_2(dmpe)_2$ (**4a**),[10]

$FeCl_2(depe)_4$ (**4b**)[10] and $FeCl_2(dprpe)_2$ (**4c**)[11] were synthesized following literature methods.

Preparations

Bis[1,2 - *bis*(*dimethylphosphino*)*ethane*]*bisazidoiron* (II) (**2a**). Method (a). Sodium azide (200 mg, 1.86 mmol) was added to a solution of $FeH_2(dmpe)_2$ (**1a**), (300 mg, 0.83 mmol) dissolved in methanol (40 cm^3) under a nitrogen atmosphere. The solution was stirred for 4 days at room temperature before the solvent was removed *in vacuo*. The crude product was recrystallized from toluene to yield intensely blue crystals of *trans*-$Fe(N_3)_2(dmpe)_2$ (**2a**, 214 mg, 59%). A crystal suitable for X-ray crystallography was obtained by slow evaporation of a toluene solution.

Method (b). $FeCl_2(dmpe)_2$ (**4a**) (100 mg, 0.24 mmol) was dissolved in methanol (3 cm^3) and an excess of sodium azide added (80 mg, 0.74 mmol). The solution was stirred for 12 h before the solvent was removed under reduced pressure. The residue was recrystallized from toluene to give blue crystals of *trans*-$Fe(N_3)_2(dmpe)_2$ (**2a**, 81 mg, 78%), which was identical in all aspects to the material prepared from (**1a**). M.p. 170°C (dec.) Found: C, 32.5; H, 7.5; N, 19.4. Calc. for $C_{12}H_{32}FeN_6P_4$: C, 32.7; H, 7.3; N, 19.1%. λ_{max}(nm) ($CHCl_3$) 243, 579, 666 [log ($\varepsilon/dm^3\ mol^{-1}\ cm^1$) 4.2, 2.4, 2.2]; ν_{max} (cm^{-1})(N_3) 2029 (Nujol); $\delta_{P\{H\}}$ (methanol-d_4) 65.1; $\delta_{H\{P\}}$ (benzene-d_6) 1.43 (24H, s, $C\mathit{H}_3$), 2.20 (8H, bs, $C\mathit{H}_2$); $\delta_{C\{H,P\}}$ (benzene-d_6) 14.27 ($\mathit{C}H_3$), 30.65 ($\mathit{C}H_2$).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*azidochloroiron*(II) (**5a**). $FeCl_2(dmpe)_2$ (**4a**) (50 mg, 117 μmol) was dissolved in methanol (3 cm^3) and 1 equiv. of sodium azide (13 mg, 117 μmol) was added. The solution was stirred for 24 h before the solvent was removed under reduced pressure. The residue was recrystallized from toluene to give a blue-green powder of *trans*-$Fe(N_3)Cl(dmpe)_2$ (**5a**, 36 mg, 71%). ν_{max}(cm^{-1})(N_3) 2028 (Nujol); $\delta_{P\{H\}}$(benzene-d_6) 62.5; $\delta_{H\{P\}}$ (benzene-d_6) 1.52 (12H, s, $C\mathit{H}_3$), 1.60 (12H, s, $C\mathit{H}_3$), 2.11 (4H, s, $C\mathit{H}_2$), 2.21 (4H, s, $C\mathit{H}_2$).

trans-*Bis*[1,2-*bis*(*dimethylphosphino*)*ethane*]*azidophenylacetylidoiron*(II) (**6a**). $FeCl(C{\equiv}CPh)(dmpe)_2$ (390 mg, 79 mmol) was dissolved in a mixture of methanol (20 cm^3) and tetrahydrofuran (50 cm^3) and stirred whilst sodium azide (400 mg, 6.4 mmd) was added. The reaction was monitored by ^{31}P NMR and when no starting material remained, the solvent was removed under reduced pressure. The residue was extracted with hot benzene and the solvent removed to leave *trans*-$Fe(N_3)(C{\equiv}CPh)(dmpe)_2$ (**6a**, 320 mg, 81%) as a yellow powder which was not purified further. M.p.: decomposed without melting at 240–242°C. Found: C, 48.5; H, 7.6; N, 8.4. Calc. for $C_{20}H_{37}FeN_3P_4$: C, 48.1; H, 7.5; N, 8.4%. ν_{max}(cm^{-1})(N_3) 2036 (Nujol); $\delta_{P\{H\}}$ (THF-d_8) 67.7; $\delta_{H\{P\}}$ (THF-d_8) 1.54 (12H, s, $C\mathit{H}_3$), 1.66 (12H, s, $C\mathit{H}_3$), 2.02 (8H, m, $C\mathit{H}_2$), 6.86 (3H, m, $C\mathit{H}$), 7.04 (2H, m, $C\mathit{H}$); $\delta_{C\{H,P\}}$ (THF-d_8) 15.1 ($\mathit{C}H_3$), 17.1 ($\mathit{C}H_3$), 32.0 ($\mathit{C}H_2$), 120.8 (ArC or $\mathit{C}{\equiv}C$), 124.0 (ArCH), 129.5 (ArCH), 130.6 (ArC or $\mathit{C}{\equiv}C$), 131.5 (ArCH), 132.3 (Fe—C).

Bis[1,2 - *bis*(*diethylphosphino*)*ethane*]*bisazidoiron* (II) (**2b**). $FeCl_2(depe)_2$ (**4b**), (80 mg, 0.15 mmol) was dissolved in methanol (5 cm^3) and an excess of sodium azide (20 mg, 0.32 mmol) was added. The solution was stirred for 3 h before the solvent was removed under reduced pressure. The residue was recrystallized from benzene to give dark blue-green crystals of *trans*-$Fe(N_3)_2(depe)_2$ (**2b**, 62 mg, 76%). M.p.: decomposed without melting at 158°C. Found: C, 43.2; H, 8.7; N, 15.0. Calc. for $C_{20}H_{48}FeN_6P_4$: C, 43.5; H, 8.8; N, 15.2%. ν_{max} (cm^{-1})(N_3) 2037 (Nujol); $\delta_{P\{H\}}$ (benzene-d_6) 69.7; $\delta_{H\{P\}}$ (benzene-d_6) 1.28 (24H, m, $C\mathit{H}_3$), 1.95, 2.07 (16H, m, $C\mathit{H}_2CH_3$), 2.16 (8H, s, $C\mathit{H}_2$); $\delta_{C\{H,P\}}$ (benzene-d_6) 9.5 ($\mathit{C}H_3$), 19.4 ($\mathit{C}H_2CH_3$), 21.6 ($\mathit{C}H_2$).

Bis[1,2 - *bis*(*dipropylphosphino*)*ethane*]*bisazidoiron* (II) (**2c**). $FeCl_2(dprpe)_2$ (**4a**), (40 mg, 0.07 mmol) was dissolved in methanol (4 cm^3) and an excess of sodium azide was added (12 mg, 0.19 mmol). The solution was stirred for 3 h before the solvent was removed under reduced pressure. The residue was recrystallized from benzene to give green crystals of *trans*-$Fe(N_3)_2(dprpe)_2$ (**2c**, 22 mg, 54%). M.p.: decomposed without melting at 77°C; $\delta_{P\{H\}}$ (benzene-d_6) 65.7; $\delta_{H\{P\}}$ (benzene-d_6) 1.20 (24H, m, $C\mathit{H}_3$), 1.80 (16H, m, $CH_2C\mathit{H}_2CH_3$), 2.11, 2.19 (16H, m, $C\mathit{H}_2CH_2CH_3$), 2.27 (8H, s, $C\mathit{H}_2$); $\delta_{C\{H,P\}}$ (benzene-d_6) 17.3 ($\mathit{C}H_3$), 19.0 ($CH_2\mathit{C}H_2CH_3$), 22.9 ($\mathit{C}H_2CH_2CH_3$), 29.1 ($\mathit{C}H_2$).

Reaction of bis[1,2-*bis*(*dimethylphosphino*) *ethane*]*bisazidoiron*(II) (**2a**) *with terminal acetylenes*. Sodium (1 mg, 0.04 mmol) was dissolved in methanol (3 cm^3) and phenylacetylene (100 mg, 1.0 mmol) added. This solution was added to a solution of $Fe(N_3)_2(dmpe)_2$ (**2a**, 20 mg, 0.05 mmol) in methanol (2 cm^3) at room temperature with constant stirring. After 18 h the yellow precipitate of $Fe(C{\equiv}CPh)_2(dmpe)_2$ (21 mg, 83%) was filtered from the reaction mixture. $Fe(C{\equiv}CPh)_2(dmpe)_2$ formed in this way was identical in all respects to an authentic sample.[5]

The known complexes[5b] $Fe(C{\equiv}C{-}Bu^t(dmpe)_2$ and $Fe(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C\text{-}H)_2(dmpe)_2$ were synthesized in an exactly analogous manner from $Fe(N_3)_2(dmpe)_2$ (**2a**), in yields > 80% by reaction with tert-butylacetylene and 1,4-diethynylbenzene, respectively.

Crystal structure determination

Cell constants were determined by a least-squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf–Nonius CAD-4F diffractometer with a graphite monochromator. Data were reduced and Lorentz, polarization and decomposition corrections were applied using the Enraf–Nonius structure determination package.[21] The structure was solved by heavy-atom methods and refined by full-matrix least-squares analysis with SHELX76.[22]

$Fe(N_3)_2(dmpe)_2$ (**2a**). $C_{12}H_{32}FeN_6P_4$, $M = 444.20$, monoclinic, space group $P2_1$, $a = 9.128(1)$, $b = 12.441(3)$, $c = 9.170(2)$ Å, $\beta = 93.53(1)^\circ$, $V = 1039.35$ Å^3, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $Z = 2$, $D_{\text{calc}} = 1.405$, $F(000) = 464$ $\mu = 10.34$ cm^{-1}, $R = 0.0221$, $R' = 0.0251$ for 1843 reflections with $I > 2.5\sigma(I)$. The crystals were blue in colour, the specimen chosen for study had the dimensions 0.148 × 0.30 × 0.095 mm. All non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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