The synthesis and structural characterization of linear and macrocyclic bis(dinitrosyliron) complexes supported by bis(phosphine) bridging ligands

Lijuan Li, Nada Reginato, Michael Urschey, Mark Stradiotto, and John D. Liarakos

Abstract: Reactions involving $Fe(NO)_2(CO)_2$ and the bis(phosphine) ligands bis(diphenylphosphino)methane (DPPM), bis(diphenylphosphino)acetylene (DPPA), 1,6-bis(diphenylphosphino)hexane (DPPH), and 1,4-bis(diphenylphosphino)-benzene (DPPB) have been examined. From these reactions, the mononuclear complex, $Fe(\kappa^l-DPPM)(NO)_2(CO)$ **3**, linear dinuclear species of the type $Fe_2(\mu-L)(NO)_4(CO)_2$ ($L = Ph_2PCH_2PPh_2$ **4**, $Ph_2PC \equiv CPPh_2$ **5**, $Ph_2PCH_2(CH_3)_4CH_2PPh_2$ **6**, and $Ph_2P(p-C_6H_4)PPh_2$ **7**), and macrocyclic dinuclear species of the type $Fe_2(\mu-L)_2(NO)_4$ ($L = Ph_2PCH_2PPh_2$ **8** and $Ph_2PC \equiv CPPh_2$ **9**) were isolated and spectroscopically characterized. For **4**, **5**, **8**, and **9**, the solid-state molecular structures of the products were determined by use of single-crystal X-ray diffraction techniques.

Key words: dinitrosyliron, iron nitrosyls, dinuclear macrocycles, bis(phosphine) complexes.

Résumé : On a étudié des réactions impliquant le Fe(NO)₂(CO)₂ et les ligands bis(phosphines), bis(diphénylphosphino)méthane (DPPM), bis(diphénylphosphino)acétylène (DPPA), 1,6-bis(diphénylphosphino)hexane (DPPH), et 1,4-bis(diphénylphosphino)benzène (DPPB). À partir de ces réactions on a isolé le complexe mononucléaire Fe(κ^{l} -DPPM)-(NO)₂(CO) (**3**), les espèces dinucléaires linéaires du type Fe₂(μ -L)(NO)₄(CO)₂ ($L = Ph_2PCH_2PPh_2$ (**4**); Ph₂PC=CPPh₂ (**5**); Ph₂PCH₂(CH₃)₄CH₂PPh₂ (**6**) et Ph₂P(p-C₆H₄)PPh₂ (**7**)) et les espèces dinucléaires macrocycliques de type Fe₂(μ -L)₂(NO)₄ ($L = Ph_2PCH_2PPh_2$ (**8**); Ph₂PC=CPPh₂ (**9**)) et on les a caractérisés par spectroscopie. Les structures moléculaires à l'état solide des produits **4**, **5**, **8** et **9** ont été déterminées par la technique de diffraction des rayons X par un cristal unique.

Mots clés : dinitrosylfer, nitrosyles de fer, macrocycles dinucléaires, complexes de bis(phosphine).

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Introduction

Dinitrosyliron-based compounds are known to participate in a variety of important chemical processes ranging from the transfer of molecular oxygen to alkenes or phosphines (1, 2) to the polymerization of olefins (3–6). Some nonheme iron nitrosyl complexes have also been identified as nitric oxide storage substances within biological systems; these have been detected by EPR studies, both as products

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We dedicate this article to Professor Don Arnold, in recognition of his remarkable contributions to chemical research in Canada.

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¹Corresponding author (e-mail: lli@csulb.edu). ²Corresponding author (e-mail: mark.stradiotto@dal.ca). after the biosynthetic evolution of NO in vitro and from the addition of NO to iron-centered proteins (7). As part of our ongoing study of this class of chemically and biologically important complexes, we reported on the synthesis, structural characterization, and electrochemical behavior of compounds such as **1** that are derived from the reaction of Fe(NO)₂(CO)(PR₃) with tetracyanoethylene (8–10). These molecules represent the first crystallographically characterized examples of dinitrosyliron-based complexes containing π -bound olefinic ligands. Subsequently, we have prepared and studied the non-heme iron complex, **2**, which comprises imidazole and nitrosyl ligands (Scheme 1) (11, 12).

Building upon this research, we have recently turned our focus to the preparation of both linear and macrocyclic bis-(dinitrosyliron) complexes bridged by either one or two bis-(phosphine) ligands, respectively, in the anticipation that these dinuclear species may exhibit interesting and unusual properties related to the proximal nature of the two metal fragments (13). The pioneering work of Cowie and co-workers (14), Puddephatt and co-workers (15), and others demonstrates the reactivity advantages that can be brought about by connecting late metal fragments with bridging bis(phosphine) ligands such as DPPM (DPPM = bis(diphenylphosphino)methane). Moreover, Hong and co-workers have shown that dinuclear Group Scheme 1. Substitution reactions of $Fe(NO)_2(CO)_2$, yielding 1 and 2.



10 complexes of the type $cyclo[M(\kappa^2-DPPM)]_2(\mu-DPPA)_2$ (DPPA = bis(diphenylphosphino)acetylene) exhibit interesting photoluminescent behavior (16). Despite the well-established history of dinuclear bis(phosphine) complexes in the field of inorganic chemistry, bis(dinitrosyliron) derivatives of this class are still rare, and their reactivity properties remain essentially unexplored (17).

Herein we report the synthesis and structural characterization of bis(dinitrosyliron) complexes spanned by a structurally diverse series of bis(phosphine) ligands, including: (a) DPPM; (b) DPPH (DPPH = 1,6-bis(diphenylphosphino)hexane); (c) DPPA; and (d) DPPB (DPPB = 1,4-bis-(diphenylphosphino)benzene). Depending on the reaction conditions employed, either linear diiron constructs connected by one bis(phosphine) linker, $(NO)_2FeP\sim PFe(NO)_2$ (A), or macrocyclic species spanned by two bridging ligands, $[(NO)_2Fe]_2(P\sim P)_2$ (B), are obtained.





The mononuclear complex, 3, and the linear diiron species, 4–7, were readily prepared from $Fe(NO)_2(CO)_2$ via addition of the desired bis(phosphine), as depicted in Scheme 2. For compounds 3-5, these could then be converted into the corresponding cyclic compounds 8 (from either 3 or 4) and 9 (from 5) (Scheme 3). Compounds 3-9 are air sensitive and undergo complete decomposition after several hours. Decomposition also occurs (albeit more slowly) when these complexes are stored either in degassed solvents or as pure solids under dinitrogen at ambient temperature. Interestingly, Braunstein et al. have previously observed the formation of both 3 and 8 as side products in the process of preparing Pt-Fe clusters (18), while Atkinson et al., in examining the reaction between $[Fe_2(\mu I_{2}(NO)_{4}$ and DPPM, were able to isolate compound 8 as the corresponding tetrahydrofuran-solvated complex (19). However, in both cases no X-ray crystallographic structural data were provided.

The conversion of $Fe(NO)_2(CO)_2$ into compounds 3–7 and subsequently into 8 or 9 is readily monitored by use of infrared spectroscopy; selected FT-IR data are listed in Table 1. The decrease in stretching frequencies observed for the car-



Scheme 3. Preparation of compounds 8 and 9.



bonyl and the two nitrosyl ligands in 3-7 relative to Fe(NO)₂(CO)₂ is characteristic of phosphine-substituted dinitrosyliron complexes (9). In turn, the nitrosyl stretching frequencies observed for both 8 and 9 appear at an even lower wavenumber. The macrocyclic DPPM-supported complex, 8, exhibits four distinct IR absorptions (1733, 1721, 1687, and 1668 cm⁻¹) in the solid and in solution (spectra obtained from samples dissolved in CH₂Cl₂ match previously reported values (19)), possibly arising from the interaction of the Fe(NO)₂ centers, as has been observed in other cyclic systems (19, 20). This phenomenon appears to depend on ring size, as the related ten-membered ring compound, 9, displays only two nitrosyl stretching signals (1723 and 1679 cm⁻¹) in both the solid and liquid states. Based on the observed IR frequencies, the nitrosyl groups are best described as linear, donating NO⁺ fragments (vide infra) (21, 22). The formation of 3-9 was also followed by use of NMR spectroscopy, and each of the dinuclear compounds (4-9) exhibit a single ³¹P NMR resonance in the range of 33-57 ppm, consistent with a disubstituted bis(phosphine) complex.

In an attempt to evaluate how altering the characteristics of the bridging bis(phosphine) ligand impacts the structural topology of these linear and macrocyclic bis(dinitrosyliron) complexes, an X-ray crystallographic study of compounds **4**, **5**, **8**, and **9** was conducted. Crystallographic collection and refinement parameters and selected metrical parameters ap-

Scheme 2. Generalized synthetic pathway to compounds 3–7.

 $\nu_{CO}~(cm^{-1})$ $v_{NO} \ (cm^{-1})$ Compounds $[Fe(DPPM)(NO)_2(CO)], 3$ 2014, 1994; 2005^a 1763, 1720 (s), 1700; 1761,^a 1718^a $[Fe_2(\mu-DPPM)(NO)_4(CO)_2], 4$ 2005; 2004^a 1760, 1719 (s), 1702; 1764,^a 1718^a $[Fe_2(\mu-DPPA)(NO)_4(CO)_2], 5$ 2020, 2005 1767, 1716 $[Fe_2(\mu-DPPH)(NO)_4(CO)_2], 6$ 1999 1755, 1701 1760, 1707 $[Fe_2(\mu-DPPB)(NO)_4(CO)_2], 7$ 2009, 1999 $[Fe_2(\mu-DPPM)_2(NO)_4], 8$ 1733, 1721, 1687, 1668

1723, 1679

 Table 1. Nitrosyl and carbonyl IR stretching frequencies for 3–9 (KBr pellet).

^aMeasured in THF solution.

 $[Fe_2(\mu-DPPA)_2(NO)_4], 9$

Table 2. Crystallographic collection and refinement parameters for 4, 5, 8, and 9 CH₂Cl₂.

	4	5	8	9-CH ₂ Cl ₂
Empirical formula	$C_{27}H_{22}P_2N_4Fe_2O_6$	$C_{28}H_{20}P_2N_4Fe_2O_6$	$\mathrm{C}_{50}\mathrm{H}_{44}\mathrm{P}_{4}\mathrm{N}_{4}\mathrm{Fe}_{2}\mathrm{O}_{4}$	$C_{53}H_{42}P_4N_4Fe_2O_4Cl_2$
Molecular weight	672.13	682.12	1000.47	1105.39
Description	Red needle	Dark red plate	Dark red prism	Dark red prism
Size (mm ³)	$0.42 \times 0.09 \times 0.03$	$0.3 \times 0.16 \times 0.08$	$0.25 \times 0.15 \times 0.14$	0.28 imes 0.25 imes 0.12
Temperature (K)	213(2)	213(2)	213(2)	213(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\overline{1}$	$P\overline{1}$	$P2_1/c$	$P2_1/c$
a (Å)	8.3037(1)	8.714(23)	21.2512(1)	21.3908(2)
b (Å)	10.9324(3)	9.539(28)	12.3414(1)	13.8839(1)
<i>c</i> (Å)	17.6037(2)	9.959(25)	22.2870(2)	17.8203(2)
α (°)	78.43(2)	114.52(8)	90.000	90.000
β (°)	77.318(1)	96.13(16)	112.49(1)	101.463(1)
γ (°)	82.198(2)	97.76(12)	90.000	90.000
Volume (Å ³)	1520.35(5)	734.1(34)	5400.69(7)	5186.84(8)
Ζ	2	1	4	4
D_{calcd} (g cm ⁻³)	1.468	1.543	1.230	1.416
Scan mode	ω-scans	ω-scans	ω-scans	ω-scans
<i>F</i> (000)	684	346	2064	2264
Absorption coefficient (mm ⁻¹)	1.105	1.145	0.698	0.834
θ-range (°)	1.20 to 22.50	2.29 to 27.34	1.04 to 22.50	0.97 to 22.50
Index ranges	$-10 \le h \le 10$	$-11 \le h \le 11$	$-27 \le h \le 27$	$-27 \le h \le 27$
	$-13 \leq k \leq 13$	$-12 \le k \le 12$	$-16 \le k \le 16$	$-17 \le k \le 17$
	$-21 \le l \le 21$	$-12 \le l \le 12$	$-28 \le l \le 20$	$-22 \le l \le 22$
Reflections collected	11 146	5231	31 207	28 244
Independent reflections	3892	2673	6976	6769
Data/restraints/parameters	3851/0/370	2673/0/190	6922/0/577	6763/12/656
GoF on F^2 (all)	1.011	0.938	1.120	1.017
Final R ($I > 2\sigma(I)$)	$R_1 = 0.0658;$	$R_1 = 0.0772;$	$R_1 = 0.0885;$	$R_1 = 0.1134;$
	$wR_2 = 0.1162$	$wR_2 = 0.1810$	$wR_2 = 0.2818$	$wR_2 = 0.2865$
R indices (all data)	$R_1 = 0.1384;$	$R_1 = 0.1462;$	$R_1 = 0.1201$	$R_1 = 0.1451$
	$wR_2 = 0.1466$	$wR_2 = 0.2146$	$wR_2 = 0.3163$	$wR_2 = 0.3264$
Transmittance (max., min.)	0.9098, 0.7914	0.8722, 0.1802	0.8944, 0.6976	0.8577, 0.2080
Largest diff. peak (e Å ⁻³)	0.338	0.971	2.932	2.605
Largest diff. hole (e $Å^{-3}$)	-0.302	-0.405	-0.444	-1.606

pear in Tables 2 and 3, respectively. Thermal ellipsoid plots of the refined molecular structures of the DPPM compounds, **4** and **8**, and the DPPA compounds, **5** and **9**, appear in Figs. 1 to 4, respectively.

The iron centers in all four of the crystallographically characterized compounds possess distorted tetrahedral geometries, a structural feature that is common to dinitrosyliron complexes (12, 22). The iron—iron distances in both the linear (4, ~5.2 Å; 5, ~7.6 Å) and macrocyclic (8, ~4.4 Å; 9, ~7.0 Å) compounds are all significantly longer than the

related distances found in other structurally characterized bis(dinitrosyliron) species described as possessing a metal metal bond (23). The crystallographically determined structures of the linear species, **4** and **5**, can be compared with that of $[Fe(NO)_2Cl]_2(\mu$ -DPPE) (DPPE = 1,2-bis(diphenylphosphino)ethane), where DPPE stands as a single bridge joining the two metal centers (17).

Despite the range in N-Fe-N angles $(115.6(4)^{\circ}$ to $126.5(4)^{\circ}$), all eight of the Fe(NO)₂ units in compounds **4**, **5**, **8**, and **9** exhibit "attracto" conformations (N-Fe-N > O-Fe-

	4	5	8	$9 \cdot CH_2 Cl_2$
Bond lengths (Å)				
Fe—Fe	5.21	7.60	4.35	7.01
Fe(1) - N(1)	1.693(8)	1.680(7)	1.643(9)	1.66(1)
Fe(1) - N(2)	1.654(6)	1.73(1)	1.644(8)	1.65(1)
Fe(2)—N(3)	1.675(8)	_	1.668(9)	1.67(1)
Fe(2) - N(4)	1.705(8)	_	1.644(9)	1.646(9)
N(1)—O	1.171(8)	1.169(7)	1.19(1)	1.19(1)
N(2)—O	1.175(6)	1.164(9)	1.20(1)	1.19(1)
N(3)—O	1.182(8)	_	1.18(1)	1.16(1)
N(4)—O	1.163(8)	_	1.19(1)	1.20(1)
Bond angles (°)				
Fe(1)-N(1)-O	177.8(7)	175.9(6)	174(1)	176.2(8)
Fe(1)-N(2)-O	174.8(7)	178.1(7)	168.9(8)	172.9(7)
Fe(2)-N(3)-O	175.0(7)	_	166.6(8)	174.5(9)
Fe(2)-N(4)-O	177.1(8)		177.1(9)	179.6(8)
N(1)-Fe(1)-N(2)	122.1(8)	115.6(4)	117.0(4)	120.5(4)
N(3)-Fe(2)-N(4)	118.1(9)	_	116.8(4)	126.5(4)
O-Fe(1)-O	119.9	114.1	109.6	116.4
O-Fe(2)-O	116.2		110.3	124.3

Table 3. Selected bond lengths (Å) and angles (°) for 4, 5, 8, and 9·CH₂Cl₂.

*Nitrosyl oxygen atoms.

O) (24–26). The observation of contracted Fe—N distances (~1.64 to ~1.73 Å) and lengthened N—O bonds (~1.16 to ~1.20 Å) in these complexes indicates significant ironnitrosyl multiple bond character, arising owing to appreciable back-donation from the iron fragment into the π^* -orbital on the nitrosyl ligand (22). By comparison, Ray et al. reported crystallographic data for a series of trigonal bipyramidal iron nitrosyl complexes, in which the Fe—N(O) and N—O distances are in the range of ~1.73–1.75 Å and ~1.12– 1.15 Å, respectively (27). These X-ray structural data, in addition to the observation of nearly linear Fe-N-O linkages, corroborate the IR spectroscopic results and suggest that the NO units in **4**, **5**, **8**, and **9** function as three-electron donors.

Compounds 5 and 9 represent the first examples of crystallographically characterized species containing the Fe- $(NO)_2(\mu$ -DPPA) fragment, and as such are worthy of further commentary. The "anti" orientation of the Fe(NO)₂ groups, coupled with the presence of a crystallographic inversion center, results in an interesting solid-state molecular geometry for the linear bis(dinitrosyliron) species, 5, in which ten of the non-hydrogen atoms (O(1), N(2), Fe(1), P(1), C(1), C(1A), P(1A), Fe(1A), N(2A), and O(1A)) are essentially coplanar (mean deviation from the plane ~ 0.32 Å). The nonlinear nature of the P-C=C fragment in 5 (P(1)-C(1)-C(1A)) 172.9(8)°) parallels other crystallographically characterized compounds of the type L_nM -DPPA- ML_n (28–34) and presumably arises because of steric congestion in the vicinity of the triple bond. Interestingly, such steric demands do not result in a lengthening of the alkyne bonds in either 5 (1.21(1) Å) or **9** (C(1)-C(2) 1.198(4) Å; C(3)-C(4)1.20(1) Å), which remain essentially unchanged relative to free DPPA (35).

The overall molecular structure of the macrocyclic DPPA compound, **9**, can be described as a severely twisted tenmembered ring, a geometry that is similar to $Mo_2(\mu-DPPA)_2(CO)_8$ (36), but different from the nearly planar structure found for PdPtCl₄(µ-DPPA)₂ (37). The puckering of the ring framework in 9 gives rise to a "bow-tie" orientation of the alkyne units, in which these fragments are twisted by approximately 49° with respect to one another (Fig. 5). As was observed for 5, the two P-C=C-P units in 9 exhibit concave bowing; however, one P-C=C-P fragment is only slightly bent (P(3)-C(3)-C(4) $173.9(9)^{\circ}$; P(4)-C(4)-C(3) $175.5(9)^{\circ}$), while the other exhibits more pronounced asymmetric bending (P(1)-C(1)-C(2) 170.8(9)°; P(2)-C(2)-C(1) 165.8(9)°). Upon viewing the structure of 9 down the Fe–Fe vector, it is evident that the DPPA ligands can be loosely classified as "staggered" (P(1)-C(1)-C(2)-P(2)) and "eclipsed" (P(3)-C(3)-C(4)-P(4)), with the former experiencing greater strain and subsequently more pronounced deviation from linearity than the latter. It is interesting to note that although $Mo_2(\mu$ -DPPA)₂(CO)₈ possesses similarly "staggered" and "eclipsed" DPPA ligands (36), a correlation between the degree of nonlinearity of the DPPA ligands and their relative orientation does not exist in this Mo-based system.

Experimental

General

All manipulations were carried out in an atmosphere of dry dinitrogen using freshly distilled and degassed solvents. Unless otherwise stated, all chemicals, including bis(diphenylphosphino)methane (DPPM, Aldrich), 1,6-bis-(diphenylphosphino)hexane (DPPH, Aldrich), bis(diphenylphosphino)acetylene (DPPA, Strem Chemicals), and 1,4-bis(diphenylphosphino)benzene (DPPB, Organometallics Inc.) were used as supplied. Fe(NO)₂(CO)₂ was prepared following a published procedure (38). The ¹H, ¹³C, and ³¹P NMR spectral data were acquired using either a Bruker AC-200 or AC-300 spectrometer in deuterated chloroform, unless otherwise stated. All ¹³C and ³¹P NMR spectra were recorded in proton-decoupled mode with phosphorus chem-

Fig. 1. The X-ray structure of 4, showing the atomic numbering scheme. Anisotropic thermal displacement ellipsoids are shown at the 30% probability level.

 $\cap(3)$

N(2)

P(1)

′C(1)

N(1)

Fe(1)

56

e(2) N(4)

b)C(85)

C(84)

C(76) C(75)

C(72

()0(4)

C(74)

C(26)

C(21)

C(2)

C(25)

副0(1)

C(24)

C(34)

C(33)

C(32)

C(46)

C(26)

N(1)

C(11)

C(21)

Fe(1

Č(32) P(2

C(46)

13

0(6)

C(41

C(35)

C(36)

C(31)

P(2)

0(4

0(2)

Fig. 2. The X-ray structure of 8, showing the atomic numbering scheme. Anisotropic thermal displacement ellipsoids are shown

C(16)

0(2)

ත්C(41)

Ć(42)

C(51)

P(3

0(3)

N(3

P(4

C(81)

C(82)

ical shifts externally referenced relative to 85% H₃PO₄ in D₂O. Melting and decomposition points were measured using differential scanning calorimetry performed on a DSC 2910 instrument (TA instruments). IR spectra were recorded on a Bio-Rad FTS-40 single-beam spectrometer using KBr pellets, unless otherwise stated. Mass spectra were recorded on a Micromass Quattro LC instrument using positive electrospray ionization (ESI+). Despite repeated attempts, satisfactory elemental analysis data for the compounds reported herein could not be obtained.

Fig. 3. The X-ray structure of 5, showing the atomic numbering scheme. Anisotropic thermal displacement ellipsoids are shown at the 30% probability level.



X-Ray crystallography

Crystallographic data for 4, 5, 8, and 9.CH₂Cl₂ were collected from suitable samples mounted on glass fibers. The instrument used for the collection of diffraction data was a Siemens P4 diffractometer equipped with a Siemens SMART 1K CCD Area Detector (using the program SMART) and a rotating anode using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Data processing was carried out by use of the program SAINT, while the program SADABS was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. Structures were solved by using the direct methods procedure in the Siemens SHELXTL program library and refined by fullmatrix least squares methods on F^2 . All non-hydrogen atoms, with the exception of the disordered atoms in 9.CH₂Cl₂, were refined using anisotropic thermal parameters. Hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the bonded carbon atom. Compound 5 crystallizes in the space group $P\overline{1}$ with half a molecule per asymmetric unit; the other half of the molecule may be generated by a crystallographic inversion center, resulting in the observation of only one molecule per unit cell (Z = 1). Combustion analysis, previously obtained by others (39), for compound 8 (similarly prepared in tetrahydrofuran) suggested the presence of one solvated tetrahydrofuran per molecule of 8 in the crystalline lattice. However, despite the fact that the data readily allow for a complete anisotropic refinement of the target molecule, attempts to resolve atomic positions for the disordered solvate were unsuccessful, leading to rather high values for the residual electron density and the refinement statistics. In the case of 9.CH₂Cl₂, the final refined structure involved a disordered model in which the phenyl rings containing C(20)-C(25) and C(50)-C(55) could exist in either of two orientations resulting from rotation about the P-C(ipso) bond. Based on the observed thermal displacement





ellipsoids, it was assumed that only these carbon atoms were significantly affected by this disorder process. The occupancies for each of the two orientations were each allowed to be refined as a free variable (final ratio of approximately 55:45 for both of the phenyl units). Moreover, during the refinement of 9.CH2Cl2, a disordered molecule of dichloromethane was located in the asymmetric unit. Given the magnitude, location, and number of electron density difference peaks observed in the region of the solvate, the final refined structure was based on a disordered model that involved two possible orientations generated by rotation about a fixed and non-disordered (fully occupied) central methylene carbon. The occupancies for each of the two orientations were each allowed to be refined as a free variable (final ratio of approximately 90:10). Hydrogen atoms for each unique component of the disordered phenyl and dichloromethane units were added at calculated positions with occupancy factors equal to the occupancy factor of the associated carbon atom. The hydrogen atoms were refined using a riding model with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the attached carbon (40-43).³

General preparation of compounds 3-7

Method (*a*): To an Erlenmeyer flask containing $Fe(NO)_2$ -(CO)₂ was added a suspension of the phosphine ligand in pentane at room temperature. After stirring the solution for 18 h, the precipitate generated was filtered and washed with pentane. Method (*b*): To an Erlenmeyer flask containing the

Fig. 5. Views of the crystallographically determined structure of $9 \cdot CH_2Cl_2$: (*a*) highlighting the "bow-tie" orientation of the alkyne units and (*b*) down the Fe(1)–Fe(2) vector (selected atoms omitted for clarity).



phosphine ligand in THF was added $Fe(NO)_2(CO)_2$ at room temperature. After stirring the solution for 18 h, the solvent was removed under reduced pressure and the remaining solid washed with pentane.

General preparation of compounds 8 and 9

Method (c): A solution of the reactants was filtered into a sealable tube, degassed by use of freeze-pump-thaw procedures, flame-sealed under vacuum, and subsequently heated to 75° C.

³Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 205068 (4), 205069 (5), 205070 (8), and 205071 (9·CH₂Cl₂) contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

[Fe(κ^1 -DPPM)(NO)₂(CO)] 3

Method (*a*): Fe(NO)₂(CO)₂ (0.1 mL, 0.9 mmol) and DPPM (170 mg, 0.44 mmol) in pentane (8 mL) produced **3** as bright orange-red powder (70 mg, 30%). Method (*b*): DPPM (170 mg, 0.44 mmol), Fe(NO)₂(CO)₂ (0.05 mL, 0.45 mmol), and THF (6 mL) produced **3** (160 mg, 69%), m.p. 119°C (with decomposition). IR (KBr) (cm⁻¹) v: 2014 (CO), 1994 (CO), 1763 (NO), 1720 (shoulder) (NO), 1700 (NO). IR (THF-solution) (cm⁻¹) v: 2005 (CO), 1761 (NO), 1718 (NO). ¹H NMR (200 MHz) &: 3.21 (d, 2H, ²J_{HP} = 8.7 Hz, CH₂), 7.27–7.49 (m, 20H, Ph). ¹³C NMR (50 MHz) &: 31.7 (m, CH₂), 127.9–137.6 (Ph), 221.3 (s, CO). ³¹P NMR (121 MHz) &: -25.0 (d, 1P, ²J_{PP} = 105.6 Hz), 48.0 (d, 1P, ²J_{PP} = 105.6 Hz, P-Fe).

$[Fe_2(\mu-DPPM)(NO)_4(CO)_2] 4$

Method (a): $Fe(NO)_2(CO)_2$ (0.34 mL, 3.1 mmol) was added to a suspension of DPPM (120 mg, 0.31 mmol) in pentane (10 mL). During the course of the reaction the DPPM dissolved, and a dark red - brown powder precipitated, which was filtered and washed with pentane (190 mg, 92%). Method (b): DPPM (500 mg, 1.3 mmol), Fe(NO)₂- $(CO)_2$ (0.3 mL, 2.7 mmol), and THF (10 mL) produced 4 (690 mg, 79%), m.p. 144°C (with decomposition). IR (KBr) (cm⁻¹) v: 2005 (CO), 1760 (NO), 1719 (shoulder) (NO), 1702 (NO). IR (THF-solution) (cm⁻¹) v: 2004 (CO), 1764 (NO), 1718 (NO). ¹H NMR (300 MHz, CD₂Cl₂) δ: 3.76 (t, 2H, ${}^{2}J_{\text{HP}} = 9.7$ Hz, CH₂), 7.41–7.44 (m, 20H, Ph). 13 C NMR (75 MHz) δ : 32.6 (t, ${}^{1}J_{CP} = 11.4$ Hz, CH₂), 129.3 (t, $J_{CP} =$ 5.2 Hz, C_o or C_m), 131.1 (s, C_p), 132.6 (t, $J_{CP} = 6.5$ Hz, C_m or C_o), 134.3 (t, $J_{CP} = 22.2$ Hz, C_i), 221.1 (s, CO). ³¹P NMR (121 MHz) δ: 45.6 (s). Single crystals suitable for X-ray diffraction studies were grown from pentane by slow evaporation under an atmosphere of dinitrogen.

$[Fe_2(\mu-DPPA)(NO)_4(CO)_2]$ 5

Method (*b*): DPPA (300 mg, 0.76 mmol), Fe(NO)₂(CO)₂ (0.18 mL, 1.6 mmol), and THF (6 mL) yielded **5** (370 mg, 71%). IR (KBr) (cm⁻¹) v: 2020 (CO), 2005 (CO), 1716 (NO), 1767 (NO). ¹H NMR (300 MHz) δ : 7.43–7.64 (m, 20H, Ph). ¹³C NMR (50 MHz) δ : 129.1 (d, $J_{CP} = 11.5$ Hz, C_o or C_m), 131.1 (s, C_p), 131.8 (d, $J_{CP} = 14.4$ Hz, C_m or C_o), 132.0 (d, $J_{CP} = 47.9$ Hz, C_i), 218.7 (s, C \equiv O). ¹³P NMR (121 MHz) δ : 33.1 (s). Single crystals suitable for X-ray diffraction studies were grown from pentane by slow evaporation under an atmosphere of dinitrogen.

$[Fe_2(\mu-DPPH)(NO)_4(CO)_2] 6$

Method (*b*): DPPH (500 mg, 1.2 mmol), Fe(NO)₂(CO)₂ (0.3 mL, 2.8 mmol), and THF (15 mL) produced **6** (500 mg, 56%). IR (KBr) (cm⁻¹) v: 1999 (CO), 1755 (NO), 1701 (NO). ¹H NMR (200 MHz) δ : 1.0–1.4 (m, 8H, PCH₂(CH₂)₄-CH₂P), 2.29 (m, 4H, PCH₂(CH₂)₄CH₂P), 7.40–7.42 (m, 20H, Ph). ¹³C NMR (50 MHz) δ : 24.1 (s, 2 × CH₂), 30.0 (d, ¹J_{CP} = 8.4 Hz, 2 × PCH₂), 30.5 (s, 2 × CH₂), 128.7 (d, J_{CP} = 9.5 Hz, C_o or C_m), 130.0 (s, C_p), 131.8 (d, J_{CP} = 11.8 Hz, C_m or C_o), 134.0 (d, J_{CP} = 39.6 Hz, C_i), 222.0 (s, CO). ³¹P NMR (121 MHz) δ : 49.2 (s).

$[Fe_2(\mu-DPPB)(NO)_4(CO)_2]$ 7

Method (*b*): DPPB (500 mg, 1.1 mmol), Fe(NO)₂(CO)₂ (0.27 mL, 2.5 mmol), and THF (25 mL) yielded **7** (760 mg, 94%); m.p. 301°C (with decomposition). IR (KBr pellet) (cm⁻¹) v: 2009 (CO), 1999 (CO), 1760 (NO), 1707 (NO). ¹H NMR (200 MHz) &: 7.34–7.42 (m, Ph). ¹³C NMR (50 MHz) &: 129.0 (d, $J_{CP} = 10.8$ Hz, C_o or C_m and o- C_6H_4), 130.8 (s, C_p), 132.3 (d, $J_{CP} = 24.6$ Hz, *i*- C_6H_4), 133.2 (d, $J_{CP} = 13.6$ Hz, C_m or C_o), 136.9 (d, $J_{CP} = 38.2$ Hz, C_i), 221.0 (s, CO). ³¹P NMR (121 MHz) &: 57.1 (s).

$[Fe_2(\mu-DPPM)_2(NO)_4] 8$

Method (*c*): After stirring DPPM (72 mg, 0.19 mmol) and **4** (125 mg, 0.19 mmol) in THF (6 mL) for 18 h, the solution gradually turned black. After 24 h a red crystalline product (**8**) was isolated by filtration (45 mg, 24%); these crystals were used for X-ray diffraction studies. Alternative route using method (*c*): **3** (150 mg, 0.28 mmol) in THF (5 mL) (35 mg, 13%); m.p. 167°C. IR (KBr) (cm⁻¹) v: 1733 (NO), 1721 (NO), 1687 (NO), 1668 (NO); the spectrum run in CH₂Cl₂ matches previously reported values (19). ¹H NMR (200 MHz) & 3.7 (t, ²*J*_{HP} = 6.5 Hz, 2 × CH₂), 7.5–7.3 (m, Ph, 40H). ³¹P NMR (121 MHz) & 43.5 (s). MS-MS (90:10 CH₂Cl₂/MeOH, *m/z*, (%)): 1000 ([M]⁺, 100), 970 ([M – NO]⁺, 2), 500 ([M/2]⁺, 45).

$[Fe_2(\mu-DPPA)_2(NO)_4]$ 9

Method (c): After stirring **5** (100 mg, 1.5 mmol) and DPPA (58 mg, 1.5 mmol) in THF (5 mL) for 18 h, the solution gradually turned black. After 72 h the tube was opened, the solvent removed under reduced pressure, and the remaining brown solid (**9**) washed with pentane (90 mg, 64%). Single crystals suitable for X-ray analysis were grown from CH_2Cl_2 by slow evaporation of the solvent under an atmosphere of dinitrogen. IR (KBr) (cm⁻¹) v: 1723 (NO), 1679 (NO). ¹H NMR (200 MHz) δ : 7.51–7.09 (m, Ph, 40H). ³¹P NMR (121 MHz) δ : 38.6 (s).

Summary

The results described herein demonstrate that both linear and macrocyclic organometallic complexes containing a pair of dinitrosyliron fragments spanned by either one or two bis(phosphine) ligands can be selectively prepared from $Fe(NO)_2(CO)_2$. The X-ray crystallographic characterization of four members of this series reveals that the choice of bridging bis(phosphine) ligand used in these syntheses has a profound influence on the molecular structure of the resulting diiron framework. This preliminary synthetic and structural investigation provides the groundwork for exploring the chemical, physical, and reactivity properties of this class of molecules. These studies are underway and will be the focus of future reports.

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References

- H. Li Kam Wah, M. Postel, and M. Pierrot. Inorg. Chim. Acta, 165, 215 (1989).
- V. Munyejabo, P. Guillaume, and M. Postel. Inorg. Chim. Acta, 221, 133 (1994).
- 3. D. Ballivet-Tkatchenko, M. Riveccie, and N. El-Murr. J. Am. Chem. Soc. **101**, 2763 (1979).
- D. Ballivet-Tkatchenko, C. Billard, and A. Revillon. J. Polym. Sci. 19, 1697 (1981).
- 5. D. Ballivet. J. Organomet. Chem. 124, C9 (1977).
- G.E. Gadd, M. Poliakoff, and J.J. Turner. Organometallics, 6, 391 (1987).
- B. Muller, A.L. Kleschjov, and J.C. Stoclet. Br. J. Pharmacol. 119, 1281 (1996).
- L. Li, G.D. Enright, and K.F. Preston. Organometallics, 13, 4686 (1994).
- A. Hörsken, G. Zheng, M. Stradiotto, C.T.C. McCrory, and L. Li. J. Organomet. Chem. 558, 1 (1998).
- L. Li, J.R. Morton, and K.F. Preston. Mag. Res. Chem. 33, S14 (1995).
- 11. N. Reginato, C.T.C. McCrory, D. Pervitsky, and L. Li. J. Am. Chem. Soc. **121**, 10 217 (1999).
- 12. L. Li. Comm. Inorg. Chem. 23, 335 (2002).
- (a) D.W. Stephan. Coord. Chem. Rev. 95, 42 (1989); (b) N.
 Wheatley and P. Kalck. Chem. Rev. 99, 3379 (1999).
- 14. S.J. Trepanier, B.T. Sterenberg, R. McDonald, and M. Cowie. J. Am. Chem. Soc. **121**, 2613 (1999) and refs. cited therein.
- 15. Y. Gao, M.C. Jennings, R.J. Puddephatt, and H.A. Jenkins. Organometallics, **20**, 3500 (2001) and refs. cited therein.
- D. Xu, H.J. Murfee, W.E. van der Veer, and B. Hong. J. Organomet. Chem. 596, 53 (2000).
- For a crystallographically characterized example, see: P. Guillaume, H. Li Kam Wah, and M. Postel. Inorg. Chem. 30, 1828 (1991).
- P. Braunstein and J. Richert. J. Chem. Soc., Dalton Trans. 3801 (1990).
- F.L. Atkinson, H.E. Blackwell, N.C. Brown, N.G. Connelly, J.G. Crossley, A.G. Orpen, A.L. Rieger, and P.H. Rieger. J. Chem. Soc., Dalton Trans. 3491 (1996).
- K.S. Chong, S.J. Rettig, A. Storr, and J. Trotter. Can. J. Chem. 57, 3119 (1979).
- 21. T.R. Bryar and D.R. Eaton. Can. J. Chem. 70, 1917 (1992).

- 22. W. Harrison and J. Trotter. J. Chem. Soc. A, 1542 (1971) and refs. cited therein.
- J.T. Thomas, J.H. Robertson, and E.G. Cox. Acta Cryst. 11, 599 (1958).
- G.B. Richter-Addo and P. Legzdins. Metal nitrosyls. Oxford University Press, New York. 1992. p. 81.
- 25. J.H. Enemark and R.D. Feltham. Coord. Chem. Rev. 13, 339 (1974).
- R.D. Feltham and J.H. Enemark. *In* Topics in stereochemistry. Vol. 12. *Edited by* G.L. Geoffroy. John Wiley & Sons, New York. 1981. p. 155.
- M. Ray, A.P. Bolombek, M.P. Hendrich, G.P.A. Yap, L.M. Liable-Sands, A.L. Rheingold, and A.S. Borovik. Inorg. Chem. 38, 3110 (1999).
- 28. R.J. Puddephatt. Chem. Soc. Rev. 12, 99 (1983).
- 29. M. Semmelmann, D. Fenske, and J.F. Corrigan. J. Chem. Soc., Dalton Trans. 2541 (1998).
- 30. T.M. Layer, J. Lewis, A. Martin, P.R. Raithby, and W.T. Wong. J. Chem. Soc., Dalton Trans. 3411 (1992).
- 31. C.J. Adams, M.I. Bruce, B.W. Skelton, and A.H. White. J. Organomet. Chem. **447**, 91 (1993).
- 32. J. Lee, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, and A.H. White. Organometallics, **12**, 3468 (1993).
- 33. G. Hogarth and T. Norman. J. Chem. Soc., Dalton Trans. 1077 (1996).
- E. Louattani, J. Suades, K. Urtiaga, M.I. Arriortua, and X. Solans. Organometallics, 15, 468 (1996).
- 35. J.C.J. Bart. Acta Cryst. B25, 489 (1969).
- 36. G. Hogarth and T. Norman. Polyhedron, 15, 2859 (1996).
- H.C. Clark, G. Ferguson, P.N. Kapoor, and M. Parvez. Inorg. Chem. 24, 3924 (1985).
- 38. W. Hieber and H.Z. Beutner. Anorg. Allg. Chem. **320**, 101 (1963).
- R.J. Mawby, D. Morris, E.M. Thorteinson, and F. Basolo. Inorg. Chem. 5, 27 (1966).
- G.M. Sheldrick. 1996. SMART [computer program]. Release 4.05. Siemens Energy And Automation Inc., Madison, WI 53719.
- G.M. Sheldrick. 1996. SAINT [computer program]. Release 4.05. Siemens Energy And Automation Inc., Madison, WI 53719.
- 42. G.M. Sheldrick. 1996. SADABS (Siemens area detector absorption corrections) [computer program].
- G.M. Sheldrick. 1994. Siemens SHELXTL [computer program]. Version 5.03. Siemens Crystallographic Research Systems, Madison, WI 53719.