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Assembling Capacity of P/N Ligands Derived from Bicyclic Aminophosphoranes: Obtaining Di- and Trimetallic Iron Nitrosyls

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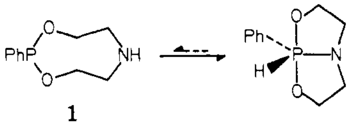
Bicyclic aminophosphorane 2, $Ph\underbrace{PH(OCH_2CH_2)_2N}$, displaces one or two carbonyl groups of $Fe(CO)_2(NO)_2$ to yield P-only-bonded adducts 4 and 5 of the monocyclic open form 1, $PhP(OCH_2CH_2)_2NH$. These adducts further react through their uncoordinated NH sites with $[Fe(NO)_2I]_2$ to yield di- and trimetallic iron nitrosyl compounds 10 and 11 in high yields.

Introduction

Polydentate ligands are a means of assembling several metallic centers in the same molecule. Cooperative effects in reactivity and catalysis might be expected from such assemblages.[1] Particularly attractive in this respect are dissymetric ligands that display donor sites of strongly distinctive character.[2] This is the situation in the open eight-membered cyclic aminophosphane tautomer 1 of bicyclic phosphorane 2.[3] In this paper we report the synthesis of di- and trimetallic species resulting from the sequential coordination of the P- and N-donor sites of ligand 1 on two distinct metallic centers.



1 2

Compounds such as 1 have already proven to be versatile ligands, capable of behaving as P-bonded monodentate or as chelated bidentate ligands.[4,5] It was also shown that in the complexes previously investigated, these ligands were prone to facile subsequent reactions that led to marked alterations of their molecular architecture. In particular, deprotonation at nitrogen afforded the first compounds in which directly bonded phosphorus and oxygen atoms,[6] or phosphorus and nitrogen atoms,[7] were *both* coordinated to the same transition metal. The reversible transfer of the phenyl group from phosphorus to a coordinated iron atom was also observed,[8] while the reaction of 2 with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ gave several products, one of them resulting from the unusual substitution of a carbonyl ligand with retention of the metal–metal triple bond.[9] To test the bridging ability of ligand 1, it was desirable to select metallic fragments that when bonded to phosphorus, should not favor such transformations.

Our current interest in iron nitrosyl complexes[10] led us to select iron dinitrosyl dicarbonyl, $Fe(CO)_2(NO)_2$, 3, as a likely candidate to meet this criterion. In the light of previous results,[11,12] stable compounds resulting from its reactions with 1 were expected to arise from the coordination of the P-donor site. Furthermore, according to its documented reactivity in substitution reactions,[11,13] the sequential coordination of one and then two molecules of 1 could be contemplated to afford substrates for the synthesis of di- and trimetallic derivatives.

Our choice of iron nitrosyls as substrates to test the assembling abilities of these ligands was also motivated by the potential interest of such derivatives in homogenous catalysis,[14] especially in relation to the environmental control of the nitric oxides produced in fossil fuel combustion. Mixed nitrosyl/carbonyl derivatives might also be useful in Fischer–Tropsch and water-gas shift reactions, in which iron carbonyl compounds have already been proven to be active.[15] Finally, there seems to be little information available yet on polynuclear nitrosylmetal compounds.[16]

Experimental Section

All the reactions were carried out under an argon atmosphere or under vacuum. Standard techniques for the handling of air- and moisture-sensitive materials were used throughout. NMR spectra were recorded on a Bruker WH-90 spectrometer operating

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Table I. IR Data[a] for Mono- and Polymetallic Iron Nitrosyl Complexes

compd[b]	ν(CO)	ν(NO)	ν(NH)	solvent	ref
$Fe(NO)_2(CO)(1)$ (4)	2020 (s)	1765 (s), 1730 (vs)	3400 (w)	CH_2Cl_2	*c*
	2020 (s)	1760 (s), 1720 (vs)	3400 (w)	KBr	*c*
$Fe(NO)_2(CO)[P(C_6H_5)_3]$ (6)	2009 (s)	1764 (s), 1722 (vs)		C_2Cl_4	13
$Fe(NO)_2(1)_2$ (5)		1725 (s), 1675 (vs)		CH_2Cl_2	*c*
		1705 (s), 1660 (vs)	3400 (w) 3300 (w)	KBr	*c*
$Fe(NO)_2[P(C_6H_5)_3]_2$ (7)		1724 (s), 1679 (vs)		C_2Cl_4	13
$Fe(NO)_2(CO)\{(1)[Fe(NO)_2I]\}$ (10)	2025 (s)	1800 (s), 1770 (s) 1740 (sh), 1730 (vs)		CH_2Cl_2	*c*
		1800 (sh), 1790 (s), 1725 (vs)		THF	*c*
$Fe(NO)_2\{(1)\ [Fe(NO)_2I]\}_2$ (11)		1800 (s, 1735 (vs), 1685 (s)		CH_2Cl_2	*c*
		1785 (s), 1725 (vs), 1685 (vs)		THF	*c*

[a] ν in cm^{-1}. s = strong; vs = very strong; w = weak; sh = shoulder. [b] (1) = $PhP(OCH_2CH_2)_2NH$. [c] This work.

at 36.44 MHz for phosphorus (85% H_3PO_4 external reference); positive chemical shifts were taken downfield from the reference. Infrared spectra were obtained on a Perkin-Elmer 577 spectrometer calibrated with polystyrene film. Elemental analyses were performed by the Service Central d'Analyses du CNRS. Mass spectra were obtained on a NERMAG-R-1010 and on a 7070E V.G. analytical mass spectrometer.

Melting points were recorded in sealed capillary tubes under argon. Solvents were purified before use: CH_2Cl_2 was distilled over P_2O_5, THF over benzophenone/Na, and hexane, heptane, and toluene over Na/K. Bicyclophosphorane **2**,[3] $Fe(CO)_2(NO)_2$ (**3**),[17] and $[Fe(NO)_2I]_2$ (**8**)[18,19] were prepared as described in the literature.

$Fe(NO)_2(CO)[PhP(OCH_2CH_2)_2NH]$ (4). A solution of the bicyclic phosphorane **2** (2.44 g, 1.15 × 10^{-2} mol) and iron dinitrosyl dicarbonyl (**3** 2.75 g, 1.6 × 10^{-2} mol) in 100 mL of hexane was maintained at 60 °C for 8 h with stirring. After being cooled to room temperature, the solution was separated by filtration from the solid that had formed. The filtrate was evaporated to dryness under vacuum. The residual red oil was purified by column chromatography on silica mounted in CH_2Cl_2. The product was eluted with acetone–dichloromethane (1:9). The red oil obtained after complete removal of the solvent under vacuum was redissolved in heptane. After 3 days at −40 °C, **4** was obtained as red needles (2.4 g, 60%): mp 35–40 °C; mass spectrum (chemical ionization, NH_3), $[m + 1]^+$ 356. Anal. Calcd for $C_{11}H_{15}N_3O_5PFe$: C, 37.2; H, 3.95; N, 11.83; P, 8.74. Found: C, 37.1; H, 3.94; N, 11.96; P. 8.54.

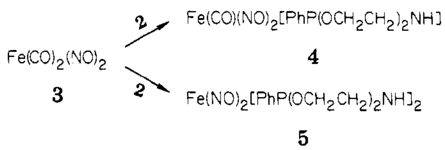
$Fe(NO)_2[PhP(OCH_2CH_2)_2NH]_2$ (5). A solution of the bicyclic phosphorane **2** (8.79 g, 4.2 × 10^{-2} mol) and iron dinitrosyl dicarbonyl (**3**, 3.1 g, 1.8 × 10^{-2} mol) in 200 mL of toluene was heated at reflux with stirring. IR monitoring indicated no further change in the composition of the solution after 6 h. The solvent was removed under vacuum, and the reddish solid residue was washed with 3 × 30 mL of pentane. Recrystallization in dichloromethane–heptane (1:4) afforded **5** as a microcrystalline dark orange solid (9.3 g, 96%): mp 119–120 °C; mass spectrum (chemical ionization, NH_3), $[m + 1]^+$ 539. Anal. Calcd for $C_{20}H_{28}N_4O_6P_2Fe$: C, 44.60; H, 5.20; N, 10.40; P, 11.52. Found: C, 44.59; H, 5.22; N, 9.66; P, 10.80.

Bimetallic Adduct $Fe(NO)_2(CO)[PhP(OCH_2CH_2)_2N(H)$-$Fe(NO)_2I]$ (10). Iron dinitrosyl iodide dimer **8** (0.163 g, 0.34 × 10^{-3} mol) in heptane (10 mL) was added dropwise to a stirred solution of complex **4** (0.238 g, 0.67 × 10^{-3} mol) in heptane (15 mL) at room temperature. A precipitate formed instantaneously. The solid was separated and washed repeatedly with hexane to afford **10** as a brown microcrystalline powder (0.37 g, 90%): mp 105–110 °C; mass spectrum (chemical ionization, NH_3), $\{Fe(NO)_2(CO)[PhP(OCH_2CH_2)_2NH](H)]\}^+$ as the heaviest fragment $[m]^+$ 356. Anal. Calcd for $C_{11}H_{14}N_5O_7PFe_2I$: C, 22.07; H, 2.34; N, 11.70. Found: C, 22.53; H, 2.34; N, 11.70.

Trimetallic Adduct $Fe(NO)_2[PhP(OCH_2CH_2)_2N(H)Fe(NO)_2I]_2$ (11). Dimer **8** (0.6 g, 1.23 × 10^{-3} mol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of complex **5** (0.66 g, 1.22 × 10^{-3} mol) in CH_2Cl_2 (30 mL) at room temperature with magnetic stirring. Removal of the solvent under vacuum yielded a black microcrystalline air-sensitive solid that was washed repeatedly with pentane and dried under vacuum (1.05 g, 85%); mp 100 °C dec. The presence of CH_2Cl_2 in the solid was indicated in the mass spectrum by the presence of three peaks at $[m]^+$ 84, 86, and 88 in a ratio close to 9:6:1.[20] Anal. Calcd for $C_{20}H_{28}N_8O_{10}P_2Fe_3I_2 \cdot CH_2Cl_2$: C, 22.72; H, 2.71; N, 10.10; Fe, 15.15. Found: C, 22.10; H, 2.50; N, 9.90; Fe, 15.40.

Results and Discussion

(1) Selective Complexation of the Phosphorus Donor Site of Ligand 1. The reaction of $Fe(CO)_2(NO)_2$ (**3**) in hexane at 60 °C with slightly less than 1 molar equiv of bicyclophosphorane **2** affords the product of monosubstitution **4**, which is soluble. It was isolated in 60% yield as low melting (~35 °C) red needles. Small quantities of the disubstituted derivative **5** were also formed and precipitated out during the reaction. The latter product **5** is more conveniently prepared (in 96% yield) by reacting **3** with an excess of **2** in refluxing toluene. IR monitoring revealed the intermediate formation of the monosubstituted derivative **4** during the course of the reaction. Elemental analysis and mass spectra (chemical ionization with ammonia or isobutylene) are consistent with the proposed formulations. The ^{31}P NMR spectra consist of single peaks at 193 and 204 ppm for **4** and **5** respectively (solvent CH_2Cl_2). These values are within the 210–160-ppm range usually found for the resonance of the metal-bonded phosphorus atom of the open cyclophosphane form **1**,[5] strongly indicating that in **4** and **5** the phosphorus atom of **1** is bonded to iron.



IR spectroscopy is frequently used to assess the electronic properties of ligands[21] and to infer the bonding mode of NO ligands in nitrosyl complexes.[22] The ν(CO) and ν(NO) values of **4** and **5** (Table I) are very close to those of the triphenylphosphane-substituted analogues **6** and **7** that contain linear NO's.[23] This could reflect a similarity in the donor/acceptor properties of cyclophosphane **1** and

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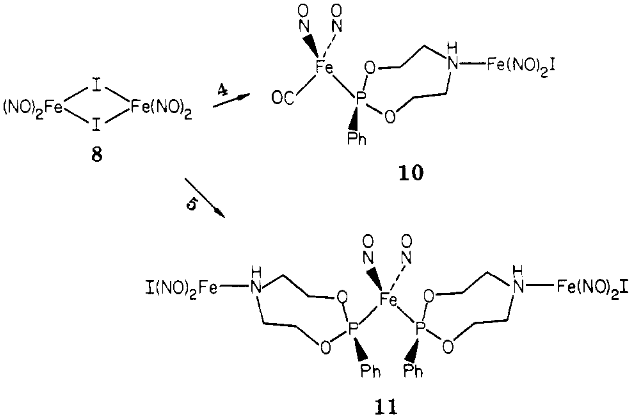
triphenylphosphane and could also indicate that the same linear arrangements and bonding modes of NO exist in both 4 and 5. One should not expect any further interaction between the metal and the amino sites, since the iron is already coordinatively saturated by the phosphorus donor site of 1. In agreement with this, concentrated solutions of 4 exhibit a weak and broad absorption centered at 3400 cm^{-1}, indicative of an uncoordinated secondary amine.[24] Such a vibration was not detected in the spectra of 5 in solution; two weak and sharp absorptions were however present at 3400 and 3300 cm^{-1}, in the spectra of 5 taken in KBr or Nujol. The appearance of more than one vibration assignable to a ν(NH) mode in the solid-state spectra of secondary amines is not uncommon[24] and might reflect the occurrence of intermolecular interactions through hydrogen bonds in the solid-state structure of **5**.

(2) Complexation of the Nitrogen-Donor Sites of Complexes 4 and 5. The ready availability of dinitrosyliron iodide dimer **8**, $[Fe(NO)_2I]_2$,[19] starting from $Fe(NO)_2(CO)_2$ and its documented reactivity toward nitrogenous bases[25,26] were the incentives to study its reactions with complexes **4** and **5**.

Reaction at room temperature of the monosubstituted derivative **4** in hexane solution with 0.5 molar equiv of dimer **8** in the same solvent resulted in the formation of the bimetallic adduct **10**, which precipitated out as a brown microcrystalline solid. Its ^{31}P NMR spectrum in CH_2Cl_2 exhibits a single peak at 202.4 ppm, about 10 ppm downfield from the phosphorus resonance of **4** in which the amino sites were not coordinated. The IR spectrum of **10** in CH_2Cl_2 shows one ν(CO) (2025 cm^{-1}) and four ν(NO) (1800, 1775, 1740 (sh), and 1730 cm^{-1}) vibrations originating from the $Fe(CO)(NO)_2$–P and $Fe(I)(NO)_2$–NH fragments. For comparison, (piperidine)$Fe(NO)_2Br$ has absorptions at 1791 and 1731 cm^{-1}.[25] A weak vibration at 3190 cm^{-1} present only in the KBr spectra was assigned to the coordinated NH on the basis of previous results with neutral monometallic molybdenum chelate complexes.[5]

The solution spectrum is solvent dependent. In THF, although the ν(CO) was only marginally affected, in the ν(NO) region only two strong, broad absorptions were present at 1790 and 1725 cm^{-1}, the third absorption at 1800 cm^{-1} being weak. This could reflect a competition between THF and the amino sites of **4** for coordinating the $Fe(NO)_2I$ fragments, an indication that the iron–nitrogen bond in **10** might be rather labile. Modification of the IR spectra of dimer **8**, when changing from CH_2Cl_2 (ν(NO) = 1810 and 1770 cm^{-1}) to THF (ν(NO) = 1780 and 1720 cm^{-1}), further substantiates the occurrence of interactions between this solvent and the $Fe(NO)_2I$ fragment.[27]

Dimer **8** also reacts with **5**. An equimolecular mixture of **8** and **5** was prepared in CH_2Cl_2. Although **5** and **8** are tractable compounds that crystallize easily when taken separately, all attempts to induce a clean crystallization from this solution were unsuccessful. However, complete removal of the solvent left behind a dark microcrystalline solid, insoluble in hexane, unlike dimer **8**, one of the initial components of the solution. Elemental analysis is consistent with the formation of the trimetallic complex **11**, retaining a solvent molecule in the solid. The ^{31}P NNR spectra of **11** in CH_2Cl_2 consists of a single and broad peak at 212–213 ppm (depending upon dilution), about 9 ppm downfield from the phosphorus resonance of **5** in the same solvent. The same result was obtained when the solution of **5** and **8** in a 1:1 ratio was prepared directly in the NMR tube. The modification of the δ(P) values resulting from the complexation of the nitrogens of **4** and **5** were thus of comparable magnitude. Three ν(NO) were present at 1800, 1735, and 1685 cm^{-1}, in the IR spectra of trimetallic **11** (in CH_2Cl_2), with the absorption at 1800 cm^{-1} only slightly stronger than the one at 1685 cm^{-1}, both of them being weaker than the 1735-cm^{-1} vibration.



Paralleling the behavior of bimetallic **10** in THF, partial decomplexation of the $Fe(NO)_2I$ unit from the N-donor sites of **5** was indicated by the disappearance of the absorption at 1800 cm^{-1} in this solvent.

Interestingly, although complex **5** is moderately air stable in the solid, the trimetallic adduct **11** is highly sensitive to molecular oxygen. The reaction resulted in the disappearance of the IR absorptions characteristic of all the NO ligands (and particularly those associated with the $Fe(NO)_2(1)_2$ subunit) and the appearance of a strong absorption centered at 1380 cm^{-1}, in the region where absorptions of NO_2 ligands are expected.[28] This reaction is under active study.

In conclusion, the open form **1** of bicyclophosphorane **2** can serve as an assemblage between two metallic fragments. On the basis of the principles that led to the synthesis of di- and trimetallic complexes **10** and **11** in good yields, it is likely that a larger variety of polymetallics of this type can be constructed by a systematic variation of the nature of the metallic centers attached to the P- and N-donor sites of **1**.

Registry No. 2, 57680-64-5; 3, 13682-74-1; 4, 84988-35-2; 5, 84988-36-3; 8, 15002-08-1; 10, 84988-37-4; 11, 84988-38-5.

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