

# Synthesis of New Phosphido-bridged Dinitrosyliron-containing Heteronuclear Metal Complexes

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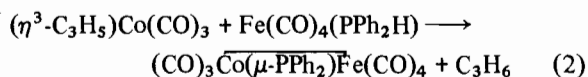
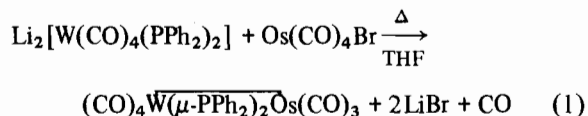
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## Abstract

New phosphido-bridged, Fe(NO)<sub>2</sub>-containing heteronuclear metal complexes have been synthesized by bridge-assisted reactions. Thus, deprotonation of Fe(NO)<sub>2</sub>(PPh<sub>2</sub>H)<sub>2</sub> with n-BuLi to Li<sub>2</sub>[Fe(NO)<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>], followed by treatment with Cp<sub>2</sub>MCl<sub>2</sub> (M = Zr, Ti), affords Cp<sub>2</sub>M(μ-PPh<sub>2</sub>)<sub>2</sub>Fe(NO)<sub>2</sub> as air-stable, purple solids. Reaction of Fe(NO)<sub>2</sub>(PPh<sub>2</sub>H)<sub>2</sub> with cobaltocene in acetonitrile at reflux gives a dark green, air-sensitive solid that is provisionally formulated as Cp<sub>2</sub>Co<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>Fe<sub>2</sub>(NO)<sub>4</sub>. Various attempts to obtain a mixed carbonyl–nitrosyl complex, (CO)<sub>3</sub>Fe(μ-PPh<sub>2</sub>)<sub>2</sub>Fe(NO)<sub>2</sub>, proved unsuccessful. All new complexes were characterized by a combination of elemental analysis, FAB mass spectrometry, and IR and <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy.

## Introduction

Bridge-assisted substitution and condensation reactions are important synthetic methodologies for heteronuclear metal complexes [1]. They have been successfully applied particularly to the preparation of a variety of phosphido-bridged heterobinuclear compounds. The syntheses in eqns. (1) and (2) provide examples of the two respective general methods [2, 3].



Whereas these methodologies have been used quite extensively in the preparation of phosphido-bridged metal carbonyl complexes, they have received much less attention in the synthesis of related metal nitrosyl complexes [4]. The study described herein was initiated in an attempt partially to fill this

apparent gap. Specifically, we set out to prepare heteronuclear μ-PPh<sub>2</sub> complexes containing the fragment Fe(NO)<sub>2</sub>. Our synthetic strategy called for the use of Fe(NO)<sub>2</sub>(PPh<sub>2</sub>X)<sub>2</sub> (X = H, Li, Cl) in conjunction with metal complexes that would be expected to participate in bridge-assisted substitution and condensation reactions with the former. The study has resulted in the isolation of new heteronuclear metal nitrosyl complexes, which are reported in this paper.

## Experimental

### General Procedures and Measurements

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of high-purity argon by using standard procedures [5]. Elemental analyses were determined by M-H-W Laboratories, Phoenix, AZ. Chromatographic separations and purifications were effected on columns packed with Florisil (100–200 mesh). Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer model 283B grating spectrophotometer or a Mattson Cygnus-25 Fourier-transform spectrometer and were calibrated with polystyrene. <sup>1</sup>H NMR spectra were obtained on a Bruker AM-250 spectrometer at ambient temperatures. <sup>31</sup>P NMR spectra were recorded on the Bruker AM-250 in the Fourier-transform mode. Chemical shifts are reported in ppm relative to 85% H<sub>3</sub>PO<sub>4</sub>. Mass spectra were obtained by use of the fast atom bombardment (FAB) technique on a Kratos MS-30 or VG 70-250S spectrometer by Mr C. R. Weisenberger or Mr David Chang.

### Materials

THF was distilled from Na and benzophenone under an atmosphere of Ar immediately before use. Other solvents were purified according to procedures described by Perrin *et al.* [6].

The ligands PPh<sub>2</sub>H and PPh<sub>2</sub>Cl and the complexes Fe(CO)<sub>5</sub>, Cp<sub>2</sub>TiCl<sub>2</sub> and Cp<sub>2</sub>Co were purchased from Strem Chemicals. Zirconocene dichloride (Cp<sub>2</sub>ZrCl<sub>2</sub>)

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was obtained from Alfa Chemicals, whereas the 1.6 M solution of n-BuLi in hexanes came from Aldrich Chemicals. All were used without further purification. The complexes  $\text{Fe}(\text{NO})_2(\text{CO})_2$  [7] and  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1.5$  dioxane [8] were prepared by the specified literature procedures.

#### Synthesis of $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{Cl})_2$

A solution of  $\text{Fe}(\text{NO})_2(\text{CO})_2$  (1.0 ml, 9.1 mmol) in THF (100 ml) in a quartz vessel under Ar was treated with  $\text{PPh}_2\text{Cl}$  (3.6 ml, 20 mmol). Gas evolution occurred immediately with the formation of  $\text{Fe}(\text{NO})_2(\text{CO})(\text{PPh}_2\text{Cl})$  as indicated by IR spectroscopy. The solution was then irradiated with 16 300-nm lamps in a Rayonet Model RPR-100 photochemical reactor until the IR  $\nu(\text{CO})$  and  $\nu(\text{NO})$  bands at 2020 and 1778  $\text{cm}^{-1}$ , respectively, of  $\text{Fe}(\text{NO})_2(\text{CO})(\text{PPh}_2\text{Cl})$  had disappeared (up to 70 h). The solvent was removed *in vacuo* to leave an oily residue. Upon addition of diethylether a red solution formed over a green oil. This solution was transferred by cannula to another flask and evaporated to dryness. The residue was triturated with diethyl ether/hexane, and the dark red, air-sensitive solid was collected by filtration, yield 5.1 g (49%), melting point (m.p.) 58–62 °C. IR (THF)  $\nu(\text{NO})$  1750s, 1708s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  155.9s ppm;  $^{31}\text{P}$  NMR (THF)  $\delta$  155.9s ppm. *Anal.* Found: C, 51.96; H, 3.87; Cl, 12.19. *Calc.*: C, 51.74; H, 3.62; Cl, 12.72%.

#### Synthesis of $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$ \*

A solution of  $\text{Fe}(\text{NO})_2(\text{CO})_2$  (0.50 ml, 4.5 mmol) and  $\text{PPh}_2\text{H}$  (1.6 ml, 9.2 mmol) in THF (100 ml) was maintained at reflux for 8 h. The solvent was removed *in vacuo*, and the red residue was dissolved in minimum THF and placed on a column of Florisil in pentane. A narrow red–brown band was eluted with pentane and gave primarily  $\text{PPh}_2\text{H}$  and  $\text{Fe}(\text{NO})_2(\text{CO})(\text{PPh}_2\text{H})$  upon evaporation of the solvent. The major dark red–brown band was then removed from the column with 10:90 diethyl ether/pentane. Concentration of the effluent and cooling at *c.* 0 °C afforded 1.6 g (71% yield) of the red–purple crystalline product. IR (THF)  $\nu(\text{NO})$  1727s, 1683s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.45–7.28m (4Ph), 6.33d ( $^1J(^{31}\text{P}^1\text{H}) = 335$  Hz, 2PH) ppm;  $^{31}\text{P}$  NMR (THF)  $\delta$  32.0d ( $^1J(^{31}\text{P}^1\text{H}) = 330$  Hz) ppm. *Anal.* Found: C, 58.84; H, 4.67. *Calc.*: C, 59.02; H, 4.51%.

The product was also obtained by photolysis of  $\text{Fe}(\text{NO})_2(\text{CO})_2$  and  $\text{PPh}_2\text{H}$  under the conditions similar to those employed for the synthesis of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{Cl})_2$ .

#### Synthesis of $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$

A solution of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  (0.20 g, 0.41 mmol) in THF (1 ml) was treated with 0.56 ml

(0.90 mmol) of 1.6 M solution of n-BuLi in hexanes at room temperature. The resulting green solution of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{Li})_2$  was added dropwise with stirring to a solution of  $\text{Cp}_2\text{ZrCl}_2$  (0.12 g, 0.41 mmol) in THF (15 ml) at –78 °C. Immediately upon addition the color of the reaction mixture turned red. Stirring was continued for 3 h at –78 °C, and then the solution was allowed to warm to room temperature. Solvent was removed *in vacuo*, and the residue was dissolved in minimum THF and chromatographed on a 2.5 × 8 cm column of Florisil eluting with diethyl ether. A red band began to move and was completely removed from the column by elution with 10:90 THF/diethyl ether. Solvent was evaporated, and the residue was recrystallized from  $\text{CH}_2\text{Cl}_2$  by slow diffusion of diethyl ether to provide 0.10 g (34% yield) of  $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  as purple needles, m.p. 270 °C (dec.). IR (THF)  $\nu(\text{NO})$  1724s, 1690s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.67–7.28m (4Ph), 5.09d ( $^3J(^{31}\text{P}^1\text{H}) = 1.4$  Hz, 2Cp) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  169.4s ppm;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  169.4s ppm; mass spectrum, *m/e* 707 ( $M^+$ ), 677 ( $M^+ - \text{NO}$ ). *Anal.* Found: C, 57.43; H, 4.08. *Calc.*: C, 57.71; H, 4.28.

#### Synthesis of $\text{Cp}_2\text{Ti}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$

To a solution of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  (0.40 g, 0.82 mmol) in 2 ml of THF was added 1.1 ml (1.8 mmol) of 1.6 M solution of n-BuLi in hexanes at *c.* 25 °C. This solution was then introduced slowly with stirring to  $\text{Cp}_2\text{TiCl}_2$  (0.20 g, 0.82 mmol) dissolved in THF (15 ml) at –78 °C. The reaction mixture was allowed to warm to room temperature over *c.* 12 h, and the solvent was removed *in vacuo*. The residue was dissolved in minimum THF and chromatographed on Florisil eluting with diethyl ether. A broad band with a black front and a purple tail was developed. The trailing part of the band (*c.* 75%) was collected and freed of the solvent. The residue was recrystallized from  $\text{CH}_2\text{Cl}_2$  by slow diffusion of hexane to yield 0.072 g (11%) of  $\text{Cp}_2\text{-Ti}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  as a purple solid, m.p. 283 °C (dec.). IR (THF)  $\nu(\text{NO})$  1725s, 1692s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.63–7.31 m (4Ph), 4.84s (2Cp) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  186.9s ppm;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  186.9s ppm; mass spectrum, *m/e* 664 ( $M^+$ ), 634 ( $M^+ - \text{NO}$ ), 599 ( $M^+ - \text{Cp}$ ), 449 ( $M^+ - \text{NO} - \text{PPh}_2$ ).

#### Reaction of $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$ with $\text{Cp}_2\text{Co}$

To a solution of  $\text{Cp}_2\text{Co}$  (0.34 g, 1.8 mmol) in acetonitrile (50 ml) was added  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  (0.41 g, 0.85 mmol) in 1 ml of THF. The reaction mixture was heated at reflux for 18 h, after which time it was cooled, filtered, and concentrated under reduced pressure. The residue was dissolved in minimum THF and chromatographed on Florisil eluting with hexane. A green band began to move

\*Developed by C. E. Shuchart, The Ohio State University, and published here with his consent.

and was completely removed from the column by elution with 10:90 diethyl ether/hexane. Solvent was evaporated to leave an air-sensitive dark green solid (0.15 g, 15% yield based on the formulation  $\text{Cp}_2\text{Co}_2(\text{PPh}_2)_2\text{Fe}_2(\text{NO})_4$ ). IR (THF)  $\nu(\text{NO})$  1749s, 1700s  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.44–7.03m (4Ph), 4.56s (2Cp) ppm;  $^{31}\text{P}\{^1\text{H}\}$  NMR (THF)  $\delta$  183.3s, br ppm;  $^{31}\text{P}$  NMR (THF)  $\delta$  183.3s, br ppm; mass spectrum,  $m/e$  851 ( $M^+ + \text{H}$ ), 835 ( $M^+ + \text{H} - \text{O}$ ).

#### Attempted Synthesis of $(\text{CO})_3\overline{\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2}$

A solution of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{Cl})_2$  (0.21 g, 0.37 mmol) in THF (10 ml) was added by cannula to a solution of  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1.5$  dioxane (0.13 g, 0.38 mmol) in THF (15 ml) at  $-78^\circ\text{C}$ . The brown reaction mixture was then allowed to warm slowly to room temperature over c. 12 h. A  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at this point showed signals at  $\delta$  155.5s (major), 50.8s (minor) and 46.1s (minor) ppm. IR  $\nu(\text{CO})$  bands were observed at 2046, 2017, 2009, 1992, 1982, 1941, 1918, 1912 and 1894  $\text{cm}^{-1}$ , and  $\nu(\text{NO})$  bands at 1761, 1747, 1741, 1728, 1705 and 1690  $\text{cm}^{-1}$ , all bands being of approximately equal intensity. Attempts to separate reaction products by chromatography on Florisil or silica gel under argon resulted in decomposition.

## Results and Discussion

The starting materials that provided a  $\text{Fe}(\text{NO})_2\text{-}(\text{PPh}_2)_2$  moiety for the construction of the desired heteronuclear metal compounds are the phosphine complexes  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{X})_2$  ( $\text{X} = \text{H}, \text{Cl}$ ). Although a number of  $\text{Fe}(\text{NO})_2(\text{phosphine})_2$  complexes have been reported [9–13],  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{Cl})_2$  could not be found in the literature, and the preparation of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  [13] is indirect and impractical. We prepared the two  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{X})_2$  complexes by treatment of  $\text{Fe}(\text{NO})_2(\text{CO})_2$  with 2 eq. of  $\text{PPh}_2\text{X}$  under thermal [11] or photochemical conditions. The products were isolated as red–purple and dark red solids whose spectroscopic properties are entirely consistent with the appropriate  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{X})_2$  formulations (see ‘Experimental’).

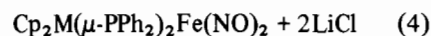
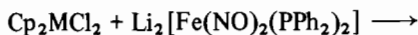
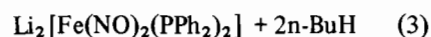
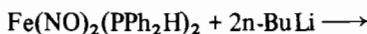
Bridge-assisted substitution reactions have been employed in the synthesis of phosphido-bridged early-late heteronuclear metal compounds [14–18]. An examination of Table 1, in which compounds of the type  $\text{Cp}_2\text{M}(\mu\text{-PR}_2)_2\text{M}'\text{L}_n$  are listed along with their  $^{31}\text{P}$  NMR chemical shifts, reveals that the late transition-metal fragment incorporates a CO, phosphine or  $\eta^5$ -indenyl ligand. Conspicuously absent are however NO-containing complexes.

We synthesized new zirconium and titanium complexes  $\text{Cp}_2\text{M}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  by the two-step procedure shown in eqns. (3) and (4).

TABLE 1.  $^{31}\text{P}$  NMR chemical shifts of phosphido-bridged early-late transition-metal complexes  $\text{Cp}_2\text{M}(\mu\text{-PR}_2)_2\text{M}'\text{L}_n$

Complex			$\delta$ (ppm)	Reference
M	M'L <sub>n</sub>	R		
Zr	W(CO) <sub>4</sub>	Ph	156.7	14
Ti	W(CO) <sub>4</sub>	Ph	196.4	14
Hf	Mo(CO) <sub>4</sub>	Et	136.8	15
Hf	Fe(CO) <sub>3</sub>	Et	160.8	15
Zr	Fe(CO) <sub>3</sub>	Ph	145.2	14
Zr	Fe(CO) <sub>3</sub>	Cy	153.7	14
Ti	Fe(CO) <sub>3</sub>	Ph	170.7	14
Zr	Fe(NO) <sub>2</sub>	Ph	169.4	this work
Ti	Fe(NO) <sub>2</sub>	Ph	186.9	this work
Hf	Rh(ind)	Ph	169.7	16
Hf	Rh(ind)	Et	169.1	16
Zr	Rh(ind)	Ph	177.3	16
Zr	Rh(ind)	Et	181.6	16
Zr	Pt(PPh <sub>3</sub> )	Ph	122.3	17
Zr	Pt(DMAD)	Ph	137.2	17
Zr	Pd(PPh <sub>3</sub> )	Ph	122.5	17
Hf	Ni(CO) <sub>2</sub>	Et	140.9	15
Zr	Ni(CO) <sub>2</sub>	Ph	163.6	17

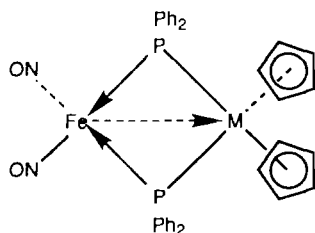
Abbreviations: cy, cyclohexyl; ind,  $\eta^5$ -indenyl; DMAD, dimethylacetylenedicarboxylate.



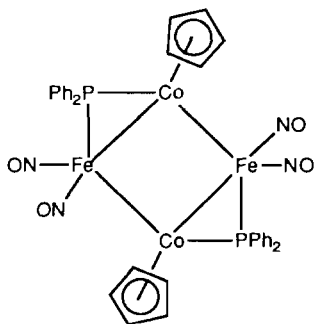
Treatment of a red solution of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  with 2 eq. of n-BuLi led to a rapid color change to green. This green solution of  $\text{Li}_2[\text{Fe}(\text{NO})_2(\text{PPh}_2)_2]$  was then slowly added to a THF solution of  $\text{Cp}_2\text{-MCl}_2$  ( $\text{M} = \text{Zr}, \text{Ti}$ ) at  $-78^\circ\text{C}$ , and the mixture was allowed to warm to room temperature. Work-up, including chromatography on Florisil, as described in ‘Experimental’, gave  $\text{Cp}_2\text{M}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  as air-stable purple solids.

The analytical data ( $\text{M} = \text{Zr}$ ) and spectroscopic properties of both  $\text{Cp}_2\text{M}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  complexes are consistent with the proposed structures. Thus, the FAB mass spectra show the occurrence of parent ion peaks and indicate loss of nitrosyl ligands. The presence of two NO ligands is reflected by the appearance of two IR  $\nu(\text{NO})$  bands in the usual region associated with  $\text{Fe}(\text{NO})_2$  groups [13]. In the  $^1\text{H}$  NMR spectra, signals occur for the Ph and Cp ( $\delta$  5.09 (Zr) and 4.84 (Ti) ppm) protons with the correct 2:1 intensity ratio.  $^{31}\text{P}$  NMR signals are observed at  $\delta$  169.4 (Zr) and 186.9 (Ti) ppm; such a low-field chemical shift would generally signify the existence of a metal–metal bond [19]. As may be seen in Table 1, other phosphido-bridged early-late transition-metal complexes of the type  $\text{Cp}_2\text{M}(\mu\text{-}$

$\text{PR}_2)_2\text{M}'\text{L}_n$  also show low-field  $^{31}\text{P}$  resonances. Whether metal-metal interaction occurs in these complexes is still an open question. The structures of  $\text{Cp}_2\text{Zr}(\mu\text{-PPh}_2)_2\text{W}(\text{CO})_4$  [14] and  $\text{Cp}_2\text{Hf}(\mu\text{-PEt}_2)_2\text{Mo}(\text{CO})_4$  [15] were determined by X-ray crystallography and shown to possess Zr-W and Hf-Mo bond distances of 3.289 and 3.400 Å, respectively. These separations are quite large; nevertheless, some metal-metal bonding interaction of the donor-acceptor type, from W to Zr and Mo to Hf, can still occur [14]. The new  $\text{Cp}_2\text{M}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  (M = Zr, Ti) complexes appear to be of a similar bonding type; their proposed structure is shown below.



Secondary phosphines react with cobaltocene to afford the phosphido-bridged complexes  $\text{Cp}_2\text{Co}_2(\mu\text{-PR}_2)_2$  [20, 21]. Following this precedent,  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  was allowed to interact with  $\text{Cp}_2\text{Co}$  in acetonitrile at reflux with the intent to synthesize a  $\mu\text{-PPh}_2\text{Co-Fe}$  complex via a bridge assisted condensation reaction. An air-sensitive dark green solid was isolated which shows a FAB mass spectral peak at  $m/e$  851, consistent with the formula  $\text{Cp}_2\text{Co}_2(\text{PPh}_2)_2\text{Fe}_2(\text{NO})_4$ \*. The  $\nu(\text{NO})$  region in the IR spectrum shows two bands of equal intensity at 1749 and  $1700\text{ cm}^{-1}$ , as expected for  $\text{Fe}(\text{NO})_2$  groups [13]. The  $^1\text{H}$  NMR spectrum contains only the Ph resonances and a Cp singlet ( $\delta$  4.56 ppm) in the approximate 2:1 ratio. The signal at  $\delta$  183.3 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum points to the presence of metal-metal bonding that supports equivalent  $\mu\text{-PPh}_2$  ligands [19]; its broad shape suggests that one of the metals forming such a bond is cobalt [23]. The following structure, in which each metal



\* $[\text{M} + \text{H}]^+$  peaks commonly occur in FAB mass spectra [22].

atom attains an 18-electron configuration, is consistent with the aforementioned spectral data. Unfortunately, we have been unsuccessful in growing crystals suitable for an X-ray diffraction study to unequivocally resolve this problem.

Since the complexes  $\text{Fe}_2(\text{CO})_6(\mu\text{-PPh}_2)_2$  and  $\text{Fe}_2(\text{NO})_4(\mu\text{-PPh}_2)_2$  have been studied rather extensively in our laboratory [24], it seemed desirable to prepare their mixed carbonyl-nitrosyl analogue,  $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$ , to complement these investigations. In that vein, a reaction was conducted between  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{Cl})_2$  and  $\text{Na}_2[\text{Fe}(\text{CO})_4] \cdot 1.5$  dioxane as described in 'Experimental'. An examination of the crude reaction mixture by  $^{31}\text{P}$  NMR spectroscopy indicated the formation of a new complex that contains  $\mu\text{-PPh}_2$  supported by a metal-metal bond [19]. However, this species decomposed during attempts at purification and isolation. We also tried to prepare  $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  by reactions of  $\text{Li}_2[\text{Fe}(\text{CO})_3(\text{PPh}_2)_2]$  with  $\text{Fe}(\text{NO})_2(\text{CO})_2$  and  $\text{Li}_2[\text{Fe}(\text{NO})_2(\text{PPh}_2)_2]$  with  $\text{Fe}(\text{CO})_4\text{I}_2$ , and by photolysis of a mixture of  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$ , but without success.

In conclusion, use of  $\text{Fe}(\text{NO})_2(\text{PPh}_2\text{H})_2$  or its deprotonated analogue,  $\text{Li}_2[\text{Fe}(\text{NO})_2(\text{PPh}_2)_2]$ , with appropriate transition-metal complexes in bridge-assisted reactions provides viable synthetic methods for phosphido-bridged,  $\text{Fe}(\text{NO})_2$ -containing heteronuclear metal compounds. However, attempts to obtain  $(\text{CO})_3\text{Fe}(\mu\text{-PPh}_2)_2\text{Fe}(\text{NO})_2$  by bridge-assisted methodologies proved unsuccessful.

## Acknowledgements

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