2020 *Organometallics* **2005,** *24,* 2020−2022

N-Heterocyclic Carbene Ligands as Cyanide Mimics in Diiron Models of the All-Iron Hydrogenase Active Site

Jean-François Capon,* Saïd El Hassnaoui, Frédéric Gloaguen,
Philippe Schollhammer, and Jean Talarmin

*UMR CNRS 6521, Chimie, Electrochimie Moléculaires et Chimie Analytique,
Faculté des Sciences, Université de Bretagne Occidentale, 6 Avenue Le Gorgeu,
C.S. 93837, 29238 Brest Cedex 3, France*

Received November 10, 2004

*Summary: The reaction of [Fe_2(μ-S(CH_2)$_3$S)$(CO)_6$] with an excess of 1,3-dimethylimidazol-2-ylidene (L_{Me}) affords the mono- and disubstituted species [Fe_2(μ-S(CH_2)$_3$S)$(CO)_5$(L_{Me})] (**1**) and [Fe_2(μ-S(CH_2)$_3$S)$(CO)_4$(L_{Me})$_2$] (**2**), respectively. The structures of **1** and **2** have been determined by X-ray crystallography.*

Extensive research on the chemistry of organometallic diiron dithiolate complexes [Fe_2(μ-S_2R)$(CO)_6$] (R = −$(CH_2)_3$−, −$CH_2NR'CH_2$−)[1] has been very recently developed in relation to the structural similarities of these synthetic species with the active site of the [FeFe] hydrogenase,[2−3] one of the enzymes which catalyze the reversible reaction $2H^+ + 2e^- \leftrightarrow H_2$.[4] Attempts to achieve closer structural models of the diiron subsite have led to the development of the cyanide chemistry of bimetallic iron species.[1] Several studies on simple and readily accessible models with a propanedithiolate bridge (−S$(CH_2)_3$S−) have been reported.[5−8] The associative substitution of two CN^- groups for carbonyls in the compound [Fe_2(μ-S(CH_2)$_3$S)$(CO)_6$] yielded the dianion [Fe_2(μ-S(CH_2)$_3$S)$(CO)_4(CN)_2$]$^{2-}$, whereas the monosubstituted cyanide derivative [Fe_2(μ-S(CH_2)$_3$S)$(CO)_5$(CN)]$^-$ could only be isolated by indirect synthesis.[5a,7a] The cyanation reaction of [Fe_2(μ-S(CH_2)$_3$S)$(CO)_6$] in the presence of trimethylphosphine afforded the complex [Fe_2(μ-S(CH_2)$_3$S)$(CO)_4$(CN)(PMe_3)]$^-$, which is an efficient catalyst for electrochemical H_2 evolution.[7] Other derivatives of the general formula [Fe_2(μ-S(CH_2)$_3$S)$(CO)_4L_2$] with L = PMe_3,[6] CNR,[7a,8a,b] P$(CH_2)_6N_3$ (1,3,5,-triaza-7-phosphaadamantane)[8c] have been reported. Protonation studies of [Fe_2(μ-S(CH_2)$_3$S)$(CO)_4L_2$] with L = PMe_3, CNR have shown that the replacement of carbonyls for better electron-donating ligands induces protonation at the diiron site, giving the μ-hydride species [Fe_2(μ-H)(μ-S(CH_2)$_3$S)$(CO)_4L_2$]$^+$.

During the past decade the use of N-heterocyclic carbene (NHC) ligands as replacements for organophosphanes in organometallic catalysts has become systematic because of their great potential in homogeneous catalysis.[9] NHCs are more than a “phosphane mimic”, as they often exhibit a greater electron-donating power than phosphine. Numerous possibilities of N functionalization induce a great structural versatility, which may be used, for example, to prepare immobilized and water-soluble catalysts. To the best of our knowledge, the use of such powerful ligands for the design of new diiron systems relevant to the active site of the [FeFe] hydrogenase has not previously been reported. We describe here our first results concerning the novel diiron N-heterocyclic carbene (NHC) complexes [Fe_2(μ-S(CH_2)$_3$S)$(CO)_5$(L_{Me})] (**1**) and [Fe_2(μ-S(CH_2)$_3$S)$(CO)_4$(L_{Me})$_2$] (**2**) (L_{Me} = 1,3-dimethylimidazol-2-ylidene).

The mono- and disubstituted NHC complexes **1** and **2** were prepared by heating in THF for 1 h at 60 °C the diiron propanedithiolate precursor [Fe_2(μ-S(CH_2)$_3$S)$(CO)_6$] in the presence of an excess of 1,3-dimethylimidazol-2-ylidene[10] (L_{Me}) (7 equiv) (Scheme 1). Complexes **1** and **2** were isolated after separation by chromatography on a silica gel column in moderate yields (12% and 50%, respectively).

Compounds **1** and **2** were characterized by IR and NMR spectroscopy and by elemental analyses. The ^1H

---

[1] (a) Darensbourg, M. Y.; Lyon, E. J.; Smee, J. J. *Coord. Chem. Rev.* **2000**, *206−207*, 533. (b) King, R. B.; Bitterwolf, T. E. *Coord. Chem. Rev.* **2000**, *206−207*, 563. (c) Darensbourg, M. Y.; Lyon, E. J.; Zhao, X.; Georgakaki, I. P. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 3683. (d) Georgakaki, I. P.; Thomson, L. M.; Lyon, E. J.; Hall, M. B.; Darensbourg, M. Y. *Coord. Chem. Rev.* **2003**, *238−239*, 255. (e) Evans, D. J.; Picket, C. J. *Chem. Soc. Rev.* **2003**, *32*, 268. (f) Rauchfuss, T. B. *Inorg. Chem.* **2004**, *43*, 14.

[2] Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853.

[3] (a) Nicolet, Y.; Piras, C.; Legrand, P.; Hatchikian, C. E.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 13. (b) Nicolet, Y.; de Lacey, A. L.; Vernede, X.; Fernandez, V. M.; Hatchikian, C. E.; Fontecilla-Camps, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 1596.

[4] Armstrong, F. A. *Curr. Opinion Chem. Biol.* **2004**, *8*, 133.

[5] (a) Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 3178. (b) Schmidt, M.; Contakes, S. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 9736. (c) Le Cloirec, A.; Best, S. P.; Borg, S.; Davies, S. C.; Evans, D. J.; Hughes, D. L.; Pickett, C. J. *Chem. Commun.* **1999**, 2285.

[6] (a) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Yarbrough, J. C.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 9710. (b) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Mejia-Rodriguez, R.; Chiang, C.-Y.; Darensbourg, M. Y. *Inorg. Chem.* **2002**, *41*, 3917. (c) Chong, D.; Georgakaki, I. P.; Mejia-Rodriguez, R.; Sanabria-Chinchilla, J.; Soriaga, M. P.; Darensbourg, M. Y. *Dalton* **2003**, *21*, 4158.

[7] (a) Gloaguen, F.; Lawrence, J. D.; Schmidt, M.; Wilson, S. R.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 12518. (b) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476. (c) Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. *Inorg. Chem.* **2002**, *41*, 6573.

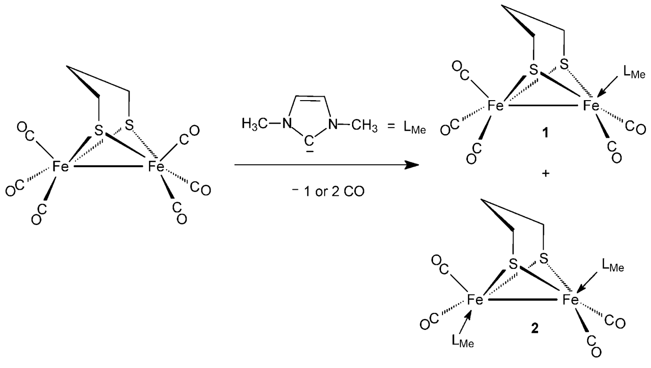
[8] (a) Lawrence, J. D.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2002**, *41*, 6193. (b) Nehring, J. L.; Heinekey, D. M. *Inorg. Chem.* **2003**, *42*, 4288. (c) Mejia-Rodriguez, R.; Chong, D.; Reibenspies, J. H.; Soriaga, M. P.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, *126*, 12004.

[9] (a) Herrmann, W. A.; *Angew. Chem., Int. Ed.* **2002**, *41*, 1290. (b) Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48*, 1. (c) Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12. (d) Jafarpour, L.; Nolan, S. P. *J. Organomet. Chem.* **2001**, *617−618*, 27. (e) Bourrisou, D.; Gueret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

[10] 1,3-Dimethylimidazol-2-ylidene was synthesized by following reported procedures, by reacting the appropriate imidazolium salt with a base, such as NaH or KO^{t}Bu; see: Arduengo, A. J., III; Dias, H. V. R.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

10.1021/om049132h CCC: $30.25

Scheme 1



NMR (CD_3CN) spectra are typical of complexes bearing a $\{Fe_2(\mu\text{-}S(CH_2)_3S)\}$ core.[11] In addition, two singlets due to the *N*-methyl (3.96 ppm (**1**) and 3.99 (**2**)) and the olefinic protons of the NHC groups (7.17 ppm (**1**) and 7.13 ppm (**2**)) are observed at room temperature. This suggests a fast rotation in solution of the NHC ligands around the Fe−C bond. Low-temperature NMR experiments were performed. The ^1H NMR spectrum of **2** in THF-d_8 at −80 °C revealed the complexity of the NHC signals and suggests the presence of more than one isomer in solution.[12]

The IR spectrum of the monosubstituted derivative **1** displays three strong bands in the carbonyl region (2036, 1971, 1912 cm^{-1}) in a frequency range slightly higher than for the monocyanide compound $[Fe_2(\mu\text{-}S(CH_2)_3S)(CN)(CO)_5]^-$ (2027−1919 cm^{-1}).[11] The three ν(CO) bands observed in the IR spectrum of **2** (1967, 1926, 1888 cm^{-1}) are very close to those reported for the bis-cyanide compound $[Fe_2(\mu\text{-}S(CH_2)_3S)(CN)_2(CO)_4]^{2-}$ (1965, 1924, 1884 cm^{-1}).[5c,8a] The ν(CO) bands are shifted to lower frequencies than those of the bis-phosphine complex $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_4(PMe_3)_2]$ (ν(CO) 1979, 1940, 1898 cm^{-1}).[6a] Overall, these IR data confirm the expected greater electron-donating ability of the NHC ligand (L_{Me}) relative to that of the trimethylphosphine[13] and the possibility to use such N-heterocyclic carbene groups as a surrogate for the cyanide ligand. The structures of complexes **1** and **2** were confirmed by X-ray analyses of single crystals obtained by cooling hexane−dichloromethane solutions (Figures 1 and 2). The Fe_2S_2 skeleton of **1** and **2** has the well-known butterfly structure found in related diiron complexes $[Fe_2(\mu\text{-}SR)_2(CO)_6]$.[5a,14] Each iron center displays approximately a square-pyramidal coordination geometry. The Fe−Fe distances in **1** (2.5126(4) Å) and **2** (2.5572(12) Å) are very close to those determined for other diiron dithiolate analogues.[5a,14] It is worth noting that the Fe−Fe distance is notably lengthened in the disubstituted species **2**.

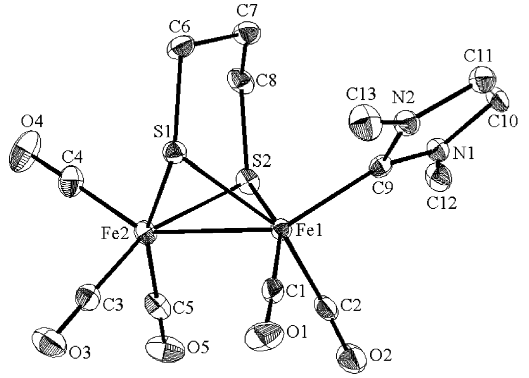


Figure 1. ORTEP view of $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_5(L_{Me})]$ (**1**), depicted with 50% thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1−Fe2 = 2.5333(7), Fe1−C1 = 1.766(4), Fe1−S1 = 2.276(1), Fe1−S2 = 2.269(1), Fe1−C9 = 1.981(3), Fe2−C4 = 1.800(4), Fe2−S1 = 2.264(1), Fe2−S2 = 2.262(1); Fe1−S1−Fe2 = 67.82(3), Fe1−S1−C6 = 114.2(1), Fe2−S1−C6 = 111.6(1), Fe1−S2−Fe2 = 67.98(3).

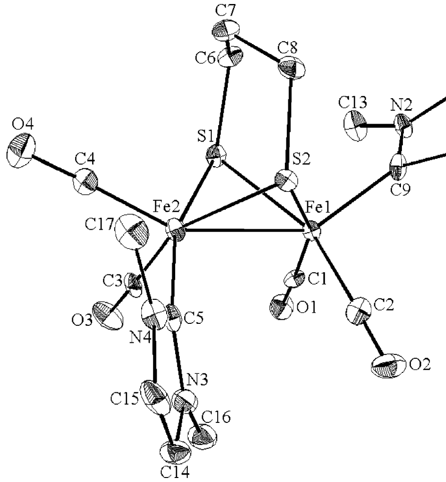


Figure 2. ORTEP view of $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_4(L_{Me})_2]$ (**2**), depicted with 30% thermal ellipsoids. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1−Fe2 = 2.5572(12), Fe1−C1 = 1.753(6), Fe1−S1 = 2.275(2), Fe1−S2 = 2.266(2), Fe1−C9 = 1.989(6), Fe2−C4 = 1.758(6), Fe2−S1 = 2.265(2), Fe2−S2 = 2.263(2); Fe1−S1−Fe2 = 68.56(5), Fe1−S1−C6 = 111.9(2), Fe2−S1−C6 = 113.3(2), Fe1−S2−Fe2 = 68.76(5).

The NHC group in **1** lies in an apical position (trans position relative to the Fe−Fe bond) in contrast with basal positions (cis to the Fe−Fe axis) of the related ligands in $[Fe_2(\mu\text{-}S(CH_2)_3S)(CN)(CO)_5]^-$ [7a] and $[Fe_2(\mu\text{-}S(CH_2)_3S)CO)_5\{C(OEt)(Ph)\}]$.[15] As expected, the Fe−C (carbene L_{Me}) distances in **1** (1.981(3) Å) and **2** (1.989(6) and 1.966(6) Å) are longer than the Fe−C (Fischer carbene) bond lengths (1.851(7) Å)[15] but compare well with Fe−C (NHC ligand) distances found in other iron complexes.[16] Solid **2** is structurally similar to the bis-cyanide complex $[Fe_2(\mu\text{-}S(CH_2)_3S)(CN)_2(CO)_4]^{2-}$: [5b] one NHC ligand lies in an apical position and the other in a basal position. Nevertheless, various isomers have been reported in the solid state for other disubstituted complexes: for example, in $[Fe_2(\mu\text{-}S(CH_2)_3S)(CN)(CO)_4$-

---

[11] Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 3268.

[12] The disubstituted derivatives $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_4L_2]$ may exist in four isomeric forms, depending on the mutual positions (basal or apical) of the substituting ligands L.[8b]

[13] (a) Öfele, K.; Kreiter, C. G. *Chem. Ber.* **1972**, *105*, 529. (b) Köcher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, *532*, 261.

[14] For recent examples, see: (a) Hogarth, G.; O'Brien, M.; Tocher, D. A. *J. Organomet. Chem.* **2003**, *672*, 29. (b) Ott, S.; Borgström, M.; Kritikos, M.; Lomoth, R.; Bergquist, J.; Åkermark, B.; Hammarström, L.; Sun, L. *Inorg. Chem.* **2004**, *43*, *4683*. (c) He, C.; Wang, M.; Zhang, X.; Wang, Z.; Chen, C.; Liu, J.; Åkermark, B.; Sun. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 3571. (d) Song, L.-C.; Yang, Z.-Y.; Bian, H.-Z.; Hu, Q.-M. *Organometallics* **2004**, *23*, 3082.

[15] Lotz, S.; Van Rooyen, P. H.; Van Dyk, M. M. *Organometallics* **1987**, *6*, 499.

[16] Buchgraber, P.; Toupet, L.; Guerchais, V. *Organometallics* **2003**, *22*, 5144.

$(PMe_3)]^{-}$ [7a] the cyanide and the phosphine ligands display apical/basal or basal/basal cis dispositions, while in $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_4(CN^tBu)_2]$[8b] only the apical/apical conformation is observed for the isocyanide ligands. In $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_4(PMe_3)_2]$ the phosphine ligands adopt a basal/basal trans disposition.[6a]

Cyclic voltammetry (CV) experiments[17] in MeCN−Bu_4NPF_6 indicated that the one-electron reduction of **1** ($E_{1/2,red}$ = −2.06 V vs Fc) exhibits some chemical reversibility, while the reduction of **2** (E_{red} = −2.47 V) is totally irreversible at scan rates lower than 0.2 V s^{-1}. In comparison to the hexacarbonyl parent (E_{red} = −1.66 V vs Fc), the replacement of one CO for one NHC leads to a negative shift of the reduction potential by about −0.4 V. This shift is significantly larger than that observed for the monosubstitution with 1,3,5-triaza-7-phosphaadamentane (about −0.2 V),[8c] for example, emphasizing the strong donating properties of the N-heterocyclic carbene ligand. As previously observed in the case of the bis-phosphine[6] and the phosphine cyanide derivatives,[7] IR and electrochemical data clearly indicate that the Fe−Fe bond in **2** is rendered sufficiently electron rich to react with electrophiles. This was confirmed by the reaction of **2** with protons (HBF_4−Et_2O) to give the bridging hydride species $\mathbf{2H}^+$, in which evidence for an Fe(μ-H)Fe linkage was provided by a positive shift of the ν(CO) bands (2050 (m), 2033 (s), 1991 (m), 1973 (s) cm^{-1}) and the hydride resonance at −19.2 ppm for the major isomer in the ^1H NMR spectra.[18] Upon addition of HBF_4−Et_2O to a MeCN−Bu_4NPF_6 solution of **2**, a new reduction peak is observed at E_{red} = −1.54 V, a potential ca. 0.9 V less negative than that for the reduction of **2**. This new electrochemical event is assigned to the reduction of $\mathbf{2H}^+$, as confirmed by a control CV of a NMR sample of $\mathbf{2H}^+$ prepared by in situ protonation of **2H** with 1 equiv of HBF_4−Et_2O. Protonation at the Fe−Fe bond typically leads to a potential shift on the order of 1 V, whereas protonation at the ligand leads to a potential shift smaller than 0.5 V.[7c] Attempted electrolysis of a solution of **2** in MeCN−Bu_4NPF_6 containing excess aqueous $HClO_4$ indicated that both **2** and $\mathbf{2H}^+$ (the formation of which was detected by CV) completely decompose over a period of several minutes.[19] Interestingly, CV of **1** in the presence of acid showed a new reduction wave at a potential ca. 0.77 V less negative than that for the reduction of the starting compound, consistent with the formation of the protonated $\mathbf{1H}^+$ species. The ^1H NMR spectrum of compound **1** in the presence of HBF_4−Et_2O exhibits hydride resonances at −13.1 and −16.1 ppm.[20] The reduction wave of $\mathbf{1H}^+$ increases with increasing acid concentrations, suggesting the catalysis of the electrochemical proton reduction. Bulk electrolysis of an acetonitrile solution of **1** in the presence of 12 equiv of $HClO_4$ consumed 8.6 F mol^{-1} over a period of about 1 h. Unfortunately, cyclic voltammetry of the solution after electrolysis revealed that the diiron complex **1** decomposed over this process.

In conclusion, this work concerns the synthesis of new bio-inspired derivatives combined with the use of powerful NHC ligands. We have synthesized the complexes $[Fe_2(\mu\text{-}S(CH_2)_3S)(CO)_{6-x}L_x]$ (x = 1, 2, L = NHC ligand) with the simple unencumbered N-heterocyclic carbene ligand 1,3-dimethylimidazol-2-ylidene as a surrogate for the cyanide ligand. Electrochemical studies suggest that the monosubstituted compound is involved in catalytic proton reduction. The IR and electrochemical data clearly show that the NHC ligands exhibit electron-donating properties superior to those of phosphane ligands and are as good a donor as the cyanide ligand. As a result, diiron compounds with NHC ligands combine the advantages of being good spectroscopic mimics of the active site of the [FeFe] hydrogenase and being amenable to modification due to the versatility of the NHC ligands.

Acknowledgment. We thank the CNRS (France, "Programme Energie-PRI 4.1") and The University of Brest (Université de Bretagne Occidentale) for financial support. We are grateful to Prof. S. Triki and Dr. F. Michaud for X-ray analyses.

Supporting Information Available: Text giving synthetic, spectroscopic, and analytical data for **1** and **2** and tables of crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049132H

---

[17] Electrochemical experiments, including cyclic voltammetry and bulk electrolysis, were carried out as described in: Capon, J.-F.; Gloaguen, F.; Schollhammer, P.; Talarmin, J. *J. Electroanal. Chem.* **2004**, *566*, 241.

[18] This is supported by the observations of hydride resonances in other μ-hydrido disubstituted derivatives of the general formula $[Fe_2(\mu\text{-}H)(\mu\text{-}S(CH_2)_3S)(CO)_4L_2]^+$ at δ −15.3 ppm with L = PMe_3,[6] at δ −14.3 to −18.7 ppm with L = CN-t-Bu,[8b] and at δ −16.1 and −19.7 ppm for L = CN^-.[6]

[19] The NMR spectrum of $\mathbf{2H}^+$ obtained by in situ protonation of **2** with HBF_4−Et_2O in 1 mL of CD_3CN displays signals corresponding to the 1,3-dimethylimidazolium salt (^1H NMR, 400 MHz, CD_3CN): δ 8.27 (s, 1H, CH), 7.26 (s, 2H, N−CHCH−N) and 3.72 (s, 6H, CH_3). This compound is probably obtained by the protonation of the carbene ligand.

[20] $\mathbf{1H}^+$ could not be isolated as a powder. A similar behavior was observed for the protonation of $[Fe_2(\mu\text{-}S(CH_3)_2(CO)_4(P(C_6H_5)_3)_2]$: Fauvel, K.; Mathieu, R.; Poilblanc, R. *Inorg. Chem.* **1976**, *15*, 976.