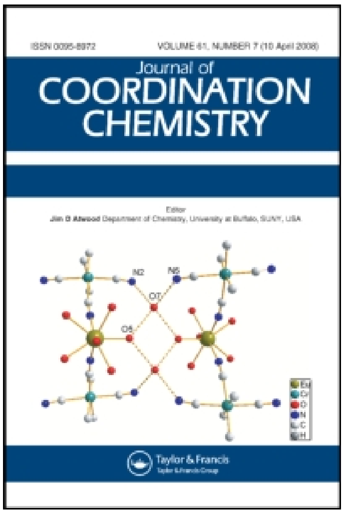

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Preparation of complexes formed in the reaction between diironnanocarbonyl and tetraalkyl(phenyl)diphosphine disulfides, $R_2P(S)P(S)R_2$ (R=Et, <i>n</i>-Pr, <i>n</i>-Bu, Ph)

Ozan Sanli Şentürk[a]
[a] Faculty of Science and Literature, Department of Chemistry, Technical University of Istanbul, Maslak, Istanbul, Turkey

To cite this Article Şentürk, Ozan Sanli(2008) 'Preparation of complexes formed in the reaction between diironnanocarbonyl and tetraalkyl(phenyl)diphosphine disulfides, $R_2P(S)P(S)R_2$ (R=Et, **<i>n</i>**-Pr, **<i>n</i>**-Bu, Ph)', Journal of Coordination Chemistry, 61: 5, 776 — 780, First published on: 13 September 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701377216

URL: http://dx.doi.org/10.1080/00958970701377216

Journal of Coordination Chemistry
Vol. 61, No. 5, 10 March 2008, 776–780

Preparation of complexes formed in the reaction between diironnanocarbonyl and tetraalkyl(phenyl)diphosphine disulfides, $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph)

OZAN SANLI ŞENTÜRK*

Faculty of Science and Literature, Department of Chemistry, Technical University of Istanbul, TR-34469, Maslak, Istanbul, Turkey

(*Received 10 February 2006; revised 23 August 2006; in final form 24 August 2006*)

$Fe_2(CO)_9$ and $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph) react to form two types of cluster complexes $Fe_3(CO)_9(\mu_3\text{-}S)_2$ (**1**), $Fe_2(CO)_6(\mu\text{-}SPR_2)_2$ (**2A**)–(**2D**), [**2A**, R = Et; **2B**, R = *n*-Pr; **2C**, R = *n*-Bu; **2D**, R = Ph]. The complexes result from phosphorus–phosphorus bond scission; in the former sulfur abstraction has also occurred. The complexes have been characterized by elemental analyses, FT-IR and $^{31}P\text{-}[^{1}H]$-NMR spectroscopy and mass spectrometry.

Keywords: Diironenneacarbonyl; Diphosphinedisulfide; Iron; Dimer

1. Introduction

Sulphido carbonyl clusters continue to attract considerable attention not only because of their fascinating structural chemistry, but also because of their ability to act as electron reservoirs and their potential in catalysis [1]. Since the preparation of the first tetraalkyldiphosphine disulfide complexes in 1965, such compounds have continued to attract attention in part because of the different possible coordination modes which the ligand may adopt [2–4]. In most cases the ligand is presumed to adopt the expected chelate bidentate coordination, $[M(CO)_4R_2P(S)P(S)R_2]$ (M = Mo and W; R = Me, Et, *n*-Pr, *n*-Bu) [5]. However, in certain cases, the ligand forms a bridge between two metals, $[M_2(CO)_{10}(R_2P(S)P(S)R_2)]$ (M = Mo and W; R = Me, Et, *n*-Pr, *n*-Bu) [6]. The series of complexes $[M(CO)_4R_2P(S)P(S)R_2]$ and $[M_2(CO)_{10}(R_2P(S)P(S)R_2)]$ (M = Mo and W; R = Me, Et, *n*-Pr, *n*-Bu) were prepared by the photochemical reaction of $M(CO)_6$ with $R_2P(S)P(S)R_2$ [5, 6]. It has been reported that the photochemical reaction of $Mn_2(CO)_{10}$ and $Me_4P_2S_2$ forms the dimethylditihiophosphinate derivative $[Mn(CO)_4(S_2PMe_2)]$ [7, 8].

The reaction between $Co_2(CO)_8$ and $Me_4P_2S_2$ was first described in 1972 and two clusters were reported [9]. Several structures were suggested based on their mass spectra but later the X-ray diffraction analysis of $Co_4(CO)_9(\mu_3\text{-}S)(\mu\text{-}PMe_2)_2$, and the disubstituted triphenylphosphine derivative of $Co_3(CO)_7(\mu_3\text{-}S)(SPMe_2)$

---

*Email: ozansanlisenturk@yahoo.co.uk

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701377216

were reported [10]. We repeated the reaction using different methods with $Me_2P(S)P(S)Me_2$ and also investigated with different alkyl groups of ligand such as (R = Et, *n*-Pr, *n*-Bu) [11]. According to two published articles [2, 3] the products, $Co_4(CO)_9(\mu_3\text{-S})(\mu\text{-PMe}_2)_2$ and $Co_3(CO)_7(\mu_3\text{-S})(SPMe_2)$, were reported but we observed another product, $Co_2(\mu\text{-CO})(\mu_4\text{-S})(CO)_{42}$, which was also obtained from the reaction of $Co_2(CO)_8$ with elemental sulfur [12].

Some years ago it was found that the mononuclear metal carbonyl $Fe(CO)_5$ reacts photochemically with $Me_2P(S)P(S)Me_2$ to cleave the P–P bond and form the complex $[(CO)_3Fe(MePS)]_2$, in which each sulfur atom bridges two Fe centres [13]. In this article we obtained $Fe_3(CO)_9(\mu_3\text{-S})_2$ (**1**) [14], $Fe_2(CO)_6(\mu\text{-SPR}_2)_2$ (**2A**)–(**2D**), **2A**, R = Et; **2B**, R = *n*-Pr; **2C**, R = *n*-Bu; **2D**, R = Ph by reaction of $Fe_2(CO)_9$ with $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph). The complexes were characterized by elemental analyses, FAB-Mass spectrometry, FT-IR and ^{31}P-NMR spectroscopy.

2. Experimental

2.1. *Measurements*

All preparations were carried out under dry nitrogen using Schlenk techniques. All solvents used in the syntheses were deoxygenated. The elemental analyses were carried out using a Carlo Erba Strummentaione Model 1106 by the Technical and Scientific Research Council of Turkey, TUBİTAK. IR spectra were recorded on samples in KBr discs at Ege University using a Mattson 1000 Fourier Transform spectrophotometer. NMR spectra were recorded in CD_2C1_2 solutions at the University of Bristol using a Jeol GX270 spectrometer. The electron-impact spectrum was recorded on a VO-Autospec instrument.

2.2. *Materials*

Pentane, benzene, hexane, dichloromethane, acetone, and silica gel were purchased from Merck, $Fe_2(CO)_9$ from Aldrich. These reagents were used as supplied. The tetraalkyldiphosphine disulfides [15, 16] were prepared by literature methods.

2.3. *Preparation of complexes*

Complexes **1** and **2A**–**2D**, were prepared by reactions of $Fe_2(CO)_9$ and $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph) and obtained in 35–45% yield by similar methods of which the following is typical.

$Fe_2(CO)_9$ (0.342 g, 1 mmol) and $Et_4P_2S_2$ (0.186 g, 1 mmol) were dissolved in diethylether (30 mL) and the reaction mixture was stirred under nitrogen overnight. At the end of the reactions, unreacted $Fe_2(CO)_9$ was not detected by FTIR. The solution was then evaporated to dryness *in vacuo*, producing a dark brown-orange mixture. The solids were dissolved in CH_2Cl_2 and separated chromatographically through a column packed with silica-gel using light petroleum (b.p. 40–60°C) as eluent. The chromatographic separation resulted in two different bands. The first band is red, **1**, the yield is 0.087 g

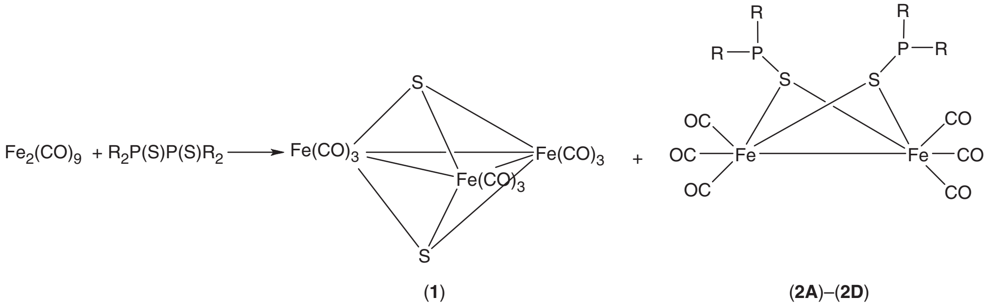

Figure 1. The reactions between $Fe_2(CO)_9$ and $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph).

Table 1. Elemental analysis results and yields of **2A**–**2D**.

Complexes[a]		Found (Calcd) (%)		
	Yield (%)	C	H	S
2A	35	32.10 (32.21)	3.77 (3.86)	12.68 (12.28)
2B	37	37.31 (37.39)	4.68 (4.88)	11.23 (11.09)
2C	27	41.75 (41.66)	5.68 (5.72)	10.07 (10.11)
2D	27	51.01 (50.45)	2.53 (2.82)	8.77 (8.98)

[a] Orange.

30%, the second band is dark yellow-orange, **2A**, the yield is 0.2247 g 35%. The complexes have been charaterized by using microanalyses, FTIR, NMR and mass spectroscopy.

3. Results and discussion

Reaction of $Fe_2(CO)_9$ in diethylether with $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph) at room temperature, produced a number of compounds as shown in figure 1. Two were seperated by column chromatography, recrystallized and isolated pure in yields which varied from 27–37%. The compound $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (**1**), has often been described in the literature [17]. The chemical composition of the air stable compounds $[Fe_2(CO)_6(\mu\text{-}SPR_2)_2]$ (**2A**)–(**2D**), were determined by elemental analysis and spectroscopic methods. Analysis data of (**2A**)–(**2D**) are given in table 1.

1 was previously reported by Hieber and Gruber [14], who allowed $HFe(CO)_4^-$ to react with sulfite ion to obtain a diamagnetic red-black crystalline compound. The compound contains the relatively common $Fe_3(\mu_3\text{-}S)_2$ core [18], **1** usually obtained from reaction between $Fe_2(CO)_9$ or $Fe(CO)_5$ and various ligands which contain sulfur donors [17]. **1** contains a seven-coordinate metal and has a distorted trigonalbipyramidal geometry [18]. The infrared spectrum possessed bands characteristic of only terminal carbonyl groups [18].

Selected infrared spectral data of **2A**–**2D** are presented in table 2. The ν(CO) IR data give no indication of the presence of bridging carbonyl. The IR spectral data in KBr for

Table 2. Selected infrared spectral bands (cm^{-1}) and ^{31}P-{^{1}H}-NMR of **2A–2D**.

Complex	ν(CO)	δP(ppm)
2A	2064m, 2026vs, 2000s, 1991w, 1968m, 1961w	65
2B	2063m, 2026vs, 1999s, 1990w, 1967m, 1961w	59
2C	2063m, 2025vs, 1998s, 1990w, 1967m, 1961w	60
2D	2067m, 2028vs, 1997s, 1990w, 1967m, 1960w	48

The ^{31}P-{^{1}H}-NMR spectra data of CD_2Cl_2 solutions of **2A–2D**, collected in table 2, show one broad signal.

Table 3. The mass spectral data of **2A–2D**.

Complex	MW	Relative intensities of the ions m/e and assignment[a]
2A	522	522(5) [M^+]; 494(7) [M^+ – (CO)]; 466(8) [M^+ – (2CO)]; 410(10) [M^+ – (4CO)]; 354(15) [M^+ – (6CO)]; 325(10) [M^+ – (6CO + Et)]; 296(15) [M^+ – (6CO + 2Et)]; 265(15) [M^+ – (6CO + 2Et + P)]; 233(40) [M^+ – (6CO + 2Et + P + S)]; 144(70) [M^+ – (6CO + 4Et + 2P + S)].
2B	578	578(9) [M^+]; 550(17) [M^+ – (CO)]; 522(12) [M^+ – (2CO)]; 494(10) [M^+ – (3CO)]; 466(10) [M^+ – (4CO)]; 438(15) [M^+ – (5CO)]; 410(10) [M^+ – (6CO)]; 324(15) [M^+ – (6CO + 2Pr)]; 261(10) [M^+ – (6CO + 2Pr + P + S)].
2C	634	634(15) [M^+]; 606(20) [M^+ – (CO)]; 550(15) [M^+ – (3CO)]; 522(10) [M^+ – (4CO)]; 466(15) [M^+ – (6CO)]; 352(15) [M^+ – (6CO + 2Bu)]; 289(11) [M^+ – (6CO + 2Bu + P + S)].
2D	715	715(18) [M^+]; 687(13) [M^+ – (CO)]; 659(12) [M^+ – (2CO)]; 631(11) [M^+ – (3CO)]; 603(15) [M^+ – (4CO)]; 575(15) [M^+ – (5CO)]; 547(10) [M^+ – (6CO)]; 330(10) [M^+ – (6CO + 2Ph + P + S)].

[a] For the mass spectral data relative intensities are given in parentheses; probable assignments in square brackets. For all assignments the most abundant isotope of Fe has been selected (^{56}Fe, 91.75%, abundant).

2A–2D showed six bands. The idealized C_{2v} symmetry of the molecule requires six C–O modes to be active. The 'butterfly' geometry rather than a planar configuration is supported by IR spectra [19]. Cleavage of the phosphorus–phosphorus bond via oxidative addition to the binuclear centre gave $Fe_2(CO)_6(\mu\text{-}SPR_2)_2$ (R = Et, *n*-Pr, *n*-Bu, Ph).

The mass spectral data of **2A–2D** are given in table 3. FAB-mass spectra show fragmentation *via* successive loss of CO and fragmentation of the organic ligands.

Symmetrical bond cleavage of the phosphorus–phosphorus, $R_2P(S)P(S)R_2$ (R = Et, *n*-Pr, *n*-Bu, Ph), bond via oxidative-addition to the binuclear centre gave complexes **2A–2D**.

Acknowledgements

We thank TUBİTAK and Research Foundation of Ege University for funds and University of Bristol for allocation of time at the NMR and Mass Spectra facilities.

References

[1] H. Vahrenkamp. In *Sulfur: Its Significance for Chemistry, fort he Geo-, Bio- and Cosmosphere and Technology*, A. Muller, B. Krebs (Eds), Elsevier, Amsterdam (1984); R.D. Adams, L.W. Yang. *J. Am. Chem. Soc.*, **105**, 235 (1983); R.D. Adams, S. Wang. *Organometallics*, **5**, 1272 (1986).
[2] K. Baker, G.W.A. Fowles. *J. Less Common Met.*, **8**, 45 (1965).
[3] H. Teichmann. *Angew. Chem., Int. Ed. Engl.*, **4**, 785 (1965).
[4] D.W. Meek, P.J. Nicpon. *J. Am. Chem. Soc.*, **87**, 4951 (1965).
[5] M.J. Almond, F. Sarikahya, O.S. Şentürk. *Polyhedron*, **16**, 1101 (1997).
[6] F. Sarıkahya, O.S. Şentürk. *Synth. React. Inorg. Met.-Org. Chem.*, **31**(10), 1843 (2001).
[7] M.J. Almond, M.G.B. Drew, F. Sarikahya, O.S. Şentürk. *Polyhedron*, **14**, 1433 (1995).
[8] G. Hoagrth, F. Sarikahya, O.S. Senturk. *Polyhedron*, **21**, 791 (2002).
[9] L. Marko, G. Bor, E. Klumpp, B. Marko, G. Almasy. *Chem. Ber.*, **96**, 55 (1963).
[10] G. Natile, S. Pignataro, G. Innorta, G. Bor. *J. Organomet Chem.*, **40**, 955 (1972).
[11] F. Sarikahya, O.S. Senturk, I. Topaloglu. *Synth. Reac. Inorg. Met.-Org. Chem.*, **30**, 1697 (2000).
[12] G. Geravasio, F. Musso, S. Vastag, G. Bor, G. Szalontai, L. Marko. *J. Cluster Sci.*, **5**, 401 (1994).
[13] G.J. Kruger, S. Lotz, L. Linford, M. Van Dyk, H.G. Raubenheimer. *J. Organometal. Chem.*, **280**, 241 (1985).
[14] W. Hieber, J. Gruber. *Z. Anorg. Allgem. Chem.*, **91**, 296 (1958).
[15] T. Moeller, H.J. Birch, N.C. Nielson. *Inorg. Synth.*, **4**, 71, (1953); S.A. Butter, Chatt. *J. Inorg. Synth.*, **15**, 186 (1974); A.I. Vogel. *Textbook of Practical Organic Chemistry*, 3rd Edn, pps. 139–145, 163–179, 193 and 280–288, Longman, London (1977); H. Nierbergall, B. Langenfeld. *Chem. Ber.*, **95**, 64 (1962).
[16] P.J. Christen, L.M. Van derLinde, F.N. Hooge. *Rec. Trav. Chim.*, **78**, 161 (1959).
[17] G. Hogarth, N.J. Taylor, A.J. Carty, A. Meyer. *J. Chem. Soc., Chem. Commun.*, 834 (1988); P.R. Raithy. In *Transition Metal Clusters*, B.F.G. Johnson (Ed.), p. 5, John Wiley, New York (1980).
[18] C.H. Wei, L.F. Dahl. *Inorg. Chem.*, **4**, 493 (1965).
[19] S.A. MacLaughin, S. Dohetry, N.J. Taylor, A.J. Carty. *Organometallics*, **11**, 4315 (1992); M.K. Anwar, G. Hogarth, O.S. Senturk, W. Clegg, S. Doherty, M.R.J. Elsegood. *J. Chem. Soc., Dalton Trans.*, 341 (2001).