



## Preparation of Complexes Formed in the Reaction Between Dicobaltoctacarbonyl and Tetraalkyldiphosphine Disulfides, $R_2P(S)P(S)R_2$ (R = Me, Et, N-Pr, N-Bu)

Fadime Uğur Sankahya , Ozan Sanli Şentürk & İşii Topaloğlu

To cite this article: Fadime Uğur Sankahya , Ozan Sanli Şentürk & İşii Topaloğlu (2000) Preparation of Complexes Formed in the Reaction Between Dicobaltoctacarbonyl and Tetraalkyldiphosphine Disulfides,  $R_2P(S)P(S)R_2$  (R = Me, Et, N-Pr, N-Bu), Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 30:9, 1697-1702, DOI: [10.1080/00945710009351862](https://doi.org/10.1080/00945710009351862)

To link to this article: <http://dx.doi.org/10.1080/00945710009351862>



Published online: 23 Apr 2008.



Submit your article to this journal [↗](#)



Article views: 9



View related articles [↗](#)



Citing articles: 2 View citing articles [↗](#)

**PREPARATION OF COMPLEXES FORMED IN THE REACTION BETWEEN  
DICOBALTOCTACARBONYL AND TETRAALKYLDIPHOSPHINE DISULFIDES,  
 $R_2P(S)P(S)R_2$  (R = Me, Et, *n*-Pr, *n*-Bu)**

Fadime Uğur (Sarıkahya)\*\*, Ozan Sanlı Şentürk<sup>a</sup> and Işıl Topaloğlu<sup>b</sup>

<sup>a</sup> Ege University, Faculty of Science, Department of Chemistry, Bornova, 35100, Izmir, Turkey

<sup>b</sup> Izmir Institute of Technology, Department of Chemistry, Çankaya, 35230, Izmir, Turkey

**ABSTRACT**

$Co_2(CO)_8$  and  $R_2P(S)P(S)R_2$  (R = Me, Et, *n*-Pr, *n*-Bu) react to form the three types of cluster complexes  $[Co_2(\mu-CO)(\mu_4-S)(CO)_4]_2$ , (**1**),  $[Co_4(CO)_8(\mu_3-S)(\mu-PR_2)_2]$  (**2A**)-(**2D**), [(**2A**), R = Me; (**2B**), R = Et; (**2C**), R = *n*-Pr; (**2D**), R = *n*-Bu] and  $[Co_3(CO)_7(\mu_3-S)(SPR_2)]$  (**3A**)-(**3D**), [(**3A**), R = Me; (**3B**), R = Et; (**3C**), R = *n*-Pr; (**3D**), R = *n*-Bu]. The structure of (**2A**) and the disubstituted triphenylphosphine derivative of (**3A**) were reported previously. The complexes have been characterized by elemental analyses, FT-IR and  $^{31}P$ -[ $^1H$ ] NMR spectroscopy and mass spectrometry.

**INTRODUCTION**

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<sup>4-6</sup>. 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)<sup>7</sup>. However, in certain cases, the ligand forms a bridging coordination between two metals,  $[M_2(CO)_{10}(R_2P(S)P(S)R_2)]$  ( $M = Mo$  and  $W$ ;  $R = Me, Et, n\text{-Pr}, n\text{-Bu}$ )<sup>8</sup>. In certain reactions fragmentation of the tetraalkyldiphosphine disulfides has been observed, the formation of, *inter alia*,  $[Me_2PS_2]^-$  ions has been reported by the reaction of OH<sup>-</sup> with  $Me_4P_2S_2$  in the chemical ionization source of a mass spectrometer<sup>9</sup>. It has been reported that the photochemical reaction of  $Mn_2(CO)_{10}$  and  $Me_4P_2S_2$  forms the dimethyldithiophosphinate derivative  $[Mn(CO)_4(S_2PMe_2)]^{10}$ .

The reaction between  $Co_2(CO)_8$  and  $Me_4P_2S_2$  was first described in 1972 and two clusters were reported<sup>2</sup>. Several structures were suggested based on their mass spectra but later the X-ray diffraction analysis of (2A),  $[Co_4(CO)_9(\mu_3-S)(\mu-PMe_2)_2]$ , and the disubstituted triphenylphosphine derivative of (3A),  $[Co_3(CO)_7(\mu_3-S)(SPPH_3)]$ , were reported<sup>3</sup>.

In this paper, we repeated these reactions using different methods and  $R_2P(S)P(S)R_2$  ( $R = Me, Et, n\text{-Pr}, n\text{-Bu}$ ). According to the two published articles<sup>2,3</sup> the products, (2A) and (3A), were reported but we observed another product,  $[Co_2(\mu-CO)(\mu_4-S)(CO)_4]_2$ , (1), which was also obtained from the reaction of  $Co_2(CO)_8$  with elemental sulphur<sup>1</sup> and that has not been reported in both articles.

## EXPERIMENTAL

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 elemental analyzer 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  $CD_2Cl_2$  solutions at the University of Bristol using a Jeol GX270 spectrometer. The electron-impact spectrum was recorded on a VO-Autospec instrument.

Pentane, benzene, hexane, dichloromethane, acetone, silicagel were purchased from Merck,  $Co_2(CO)_8$  from Aldrich. These reagents were used as supplied. The tetraalkyldiphosphine disulfides<sup>11,12</sup> were prepared by literature methods.

The complexes (1), (2A)-(2D), (3A)-(3D) were prepared by the reactions of  $Co_2(CO)_8$  and  $R_2P(S)P(S)R_2$  ( $R = Me, Et, n\text{-Pr}, n\text{-Bu}$ ) and obtained in 15-35% yield by similar methods of which the following is typical.

$\text{Co}_2(\text{CO})_8$  (0.34 g, 1 mmol) and  $\text{Me}_4\text{P}_2\text{S}_2$  (0.18 g, 1 mmol) were dissolved in benzene (30 mL) (reactions utilising the Et, *n*-Pr and *n*-Bu derivatives were performed in *n*-pentane) and the reaction mixture was stirred under nitrogen overnight. At the end of the reactions, unreacted  $\text{Co}_2(\text{CO})_8$  was not detected by FTIR. The solution was then evaporated to dryness *in vacuo*, and produced a dark brown-greenish solid. The solid was dissolved in light petroleum (b.p. 40–60 °C) 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 three different bands. The first band is pinkish-brown, (**1**), the yield is 0,087 g 15%, the second band is green, (**2A**), the yield is 0.2247 g 35%, and the third band is brown, (**3A**), the yield is 0,1743 g 35%. The complexes have been characterized by micro analyses, FTIR, NMR and mass spectroscopy.

**(1)** Found: C, 20.9%. Calcd. for  $\text{C}_{10}\text{O}_{10}\text{Co}_4\text{S}_2$  (579.8): C, 20.7%. **(2A)** Found: C, 24.7; H, 1.9%. Calcd. for  $\text{C}_{13}\text{H}_{12}\text{O}_9\text{Co}_4\text{SP}_2$  (641.8): C, 24.3; H, 1.9%. **(2B)** Found: C, 29.4; H, 2.9%. Calcd. for  $\text{C}_{17}\text{H}_{20}\text{O}_9\text{Co}_4\text{SP}_2$  (697.8): C, 29.32; H, 2.8%. **(2C)** Found: C, 33.5; H, 3.8%. Calcd. for  $\text{C}_{21}\text{H}_{28}\text{O}_9\text{Co}_4\text{SP}_2$  (753.8): C, 33.8; H, 3.7%. **(2D)** Found: C, 37.2; H, 4.7%. Calcd. for  $\text{C}_{25}\text{H}_{36}\text{O}_9\text{Co}_4\text{SP}_2$  (809.8): C, 37.0; H, 4.8%. **(3A)** Found: C, 21.8; H, 1.2%. Calcd. for  $\text{C}_9\text{H}_6\text{O}_7\text{Co}_3\text{S}_2\text{P}$  (497.9): C, 21.6; H, 1.2%. **(3B)** Found: C, 25.2; H, 1.7%. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{O}_7\text{Co}_3\text{S}_2\text{P}$  (525.9): C, 25.1; H, 1.9%. **(3C)** Found: C, 28.3; H, 2.7%. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{O}_7\text{Co}_3\text{S}_2\text{P}$  (553.9): C, 28.1; H, 2.5%. **(3D)** Found: C, 30.7; H, 3.2%. Calcd. for  $\text{C}_{15}\text{H}_{18}\text{O}_7\text{Co}_3\text{S}_2\text{P}$  (581.9): C, 30.9; H, 3.2%.

**(1)**:  $\nu(\text{CO})_t$  2083 m, 2042 s, 2021 m, 2009 m  $\text{cm}^{-1}$ ,  $\nu(\text{CO})_b$  1867 s  $\text{cm}^{-1}$ ; **(2A)**:  $\nu(\text{CO})$  2069 s, 2040 s, 2021 vs, 2013 s, 2000 m, 1985 s, 1977 s, 1930 m  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  152.52 ppm. **(2B)**:  $\nu(\text{CO})$  2063 s, 2041 s, 2025 vs, 2017 s, 1993 m, 1981 s, 1972 m, 1924 m  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  201.9 ppm. **(2C)**:  $\nu(\text{CO})$  2073 s, 2050 s, 2022 vs, 2010 s, 2001 m, 1990 m, 1978 m, 1926 m  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  190.95 ppm. **(2D)**:  $\nu(\text{CO})$  2070 s, 2048 s, 2024 vs, 2008 s, 2001 m, 1988 m, 1978 m, 1926 m  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  186.38 ppm. **(3A)**:  $\nu(\text{CO})$  2084 s, 2044 vs, 2040 vs, 2023 s, 1996 w  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  67.06 ppm. **(3B)**:  $\nu(\text{CO})$  2086 s, 2047 vs, 2041 vs, 2025 vs, 1993 w  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  56.73 ppm. **(3C)**:  $\nu(\text{CO})$  2086 s, 2047 vs, 2036 vs, 2021 vs, 1989 w  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  52.25 ppm. **(3D)**:  $\nu(\text{CO})$  2085 s, 2055 vs, 2037 vs, 2025 s, 1991 w  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR  $\delta$  53.32 ppm.

For the mass spectral data relative intensities are given in parentheses; probable assignments

in square brackets. For all assignments the most abundant isotope of Co has been selected:  $^{59}\text{Co}$  100% abundant.

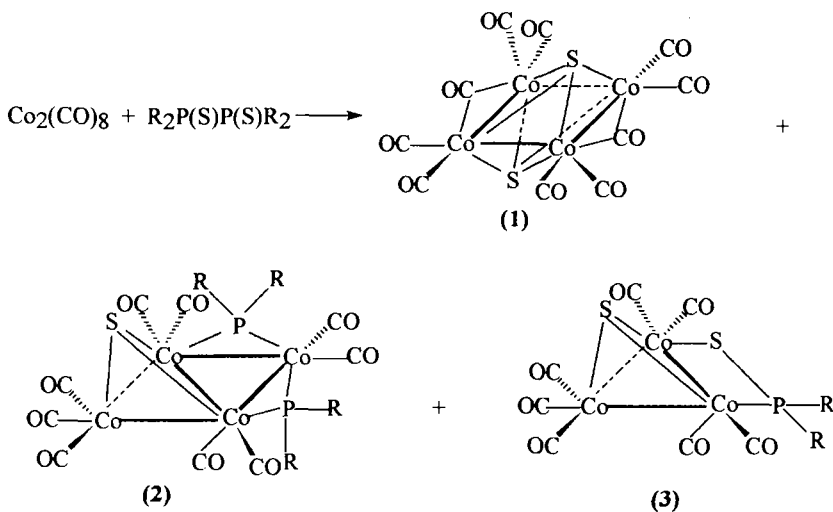
M/z: **(1)** (M. W. = 580): 468 (60) [ $\text{M}^-$ -(4CO)]; 440 (70) [ $\text{M}^-$ -(5CO)]; 412 (30) [ $\text{M}^-$ -(6CO)]. **(2A)** (M. W. = 642): 487 (10) [ $\text{M}^-$ -(5CO + Me)]; 459 (20) [ $\text{M}^-$ -(6CO + Me)]; 430 (10) [ $\text{M}^-$ -(7CO + Me)]. **(2B)** (M. W. = 698): 614 (10) [ $\text{M}^+$ -(3CO)]; 586 (50) [ $\text{M}^-$ -(4CO)]; 558 (50) [ $\text{M}^-$ -(5CO)]. **(2C)** (M. W. = 754): 670 (20) [ $\text{M}^-$ -(3CO)]; 642 (100) [ $\text{M}^-$ -(4CO)]; 614 (50) [ $\text{M}^-$ -(5CO)]. **(2D)** (M. W. = 810): 467 (25) [ $\text{M}^+$ -(3CO + 4Bu + P)]; 439 (10) [ $\text{M}^-$ -(4CO + 4Bu + P)]; 411 (5) [ $\text{M}^-$ -(5CO + 4Bu + P)]; 383 (15) [ $\text{M}^-$ -(6CO + 4Bu + P)]; 355 (10) [ $\text{M}^-$ -(7CO + 4Bu + P)]. **(3A)** (M. W. = 498): 414 (15) [ $\text{M}^-$ -(3CO)]; 359 (15) [ $\text{M}^-$ -(5CO)]. **(3B)** (M. W. = 526): 396 (100) [ $\text{M}^-$ -(3CO + Et + S)]; 368 (30) [ $\text{M}^-$ -(4CO + Et + S)]; 353 (20) [ $\text{M}^-$ -(4CO + Et + S)]; 339 (100) [ $\text{M}^-$ -(4CO + S + Et)]. **(3C)** (M. W. = 554): 470 (30) [ $\text{M}^-$ -(3CO)]; 442 (100) [ $\text{M}^-$ -(4CO)]; 414 (15) [ $\text{M}^-$ -(5CO)]; 386 (30) [ $\text{M}^-$ -(6CO)]; 358 (25) [ $\text{M}^-$ -(7CO)]. **(3D)** (M. W. = 582): 498 (30) [ $\text{M}^+$ -(3CO)]; 470 (60) [ $\text{M}^-$ -(4CO)]; 442 (40) [ $\text{M}^-$ -(5CO)]; 414 (10) [ $\text{M}^-$ -(6CO)].

## RESULTS AND DISCUSSION

The reactions between  $\text{Co}_2(\text{CO})_8$  and  $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2$  (R = Me, Et, *n*-Pr, *n*-Bu) give three types of cluster complexes:  $[\text{Co}_2(\mu\text{-CO})(\mu_4\text{-S})(\text{CO})_4]_2$ , **(1)**,  $[\text{Co}_4(\text{CO})_9(\mu_3\text{-S})(\mu\text{-PR}_2)_2]$  **(2A)-(2D)**, and  $[\text{Co}_3(\text{CO})_7(\mu_3\text{-S})(\text{SPR}_2)]$  **(3A)-(3D)** as shown in Figure 1.

Compound **(1)** was not reported as one of the three type cluster complexes by Natile and co-workers in 1972 and Geravasio and co-workers in 1994<sup>2,3</sup>, but it was previously reported in 1963 by the reaction of  $\text{Co}_2(\text{CO})_8$  with elemental sulphur by Marko *et al.* As expected, four terminal IR bands and one bridging CO band were observed due to the  $D_{2h}$  point group. The FTIR spectrum of **(1)** in hexane exhibited four carbonyl bands at 2057 vs, 2047 s, 2032 s, 1990 w  $\text{cm}^{-1}$ , together with a band in the bridging carbonyl region at 1896  $\text{cm}^{-1}$ . These bands are in accord with the previous data given in the literature<sup>1</sup>. Evidence for the stoichiometry of  $[\text{Co}_2(\mu\text{-CO})(\mu_4\text{-S})(\text{CO})_4]_2$ , **(1)**, was provided by its mass spectrum which showed fragmentation *via* successive loss of CO groups.

Although the elemental compositions and formulae of the complexes **(2A)** and **(3A)** were given by Natile and co-workers<sup>2</sup>, none of their suggested structures were correct. The structure of **(2A)** and of the disubstituted triphenylphosphine derivative of **(3A)** were determined by Geravasio and co-workers<sup>3</sup>.



A: R = Me; B: R = Et; C: R = *n*-Pr; D: R = *n*-Bu

Fig. 1. The Reactions Between  $\text{Co}_2(\text{CO})_8$  and  $\text{R}_2\text{P}(\text{S})\text{P}(\text{S})\text{R}_2$  (R = Me, Et, *n*-Pr, *n*-Bu)

Compound **(2A)** contains a quasi-planar rhomboidal  $\text{Co}_4$  cluster formed by two  $\text{Co}_3$  isosceles triangles sharing a Co-Co edge. One triangle is capped by a sulfur atom, the other triangle has two edge-bridging  $\text{PMe}_2$  moieties. Compound **(3A)** contains a  $\text{Co}_3\text{S}$  cluster with one side bridged by a  $\text{SPMe}_2$  unit forming a four-membered  $\text{Co}_2\text{SP}$  ring<sup>3</sup>.

The IR spectral data in KBr for **(2A)**–**(2D)** show eight bands. The idealized  $C_2$  symmetry of the molecule requires nine C-O modes to be active. Hence, one of the IR-active C-O stretching normal modes is absent from the spectrum, presumably owing to the coincidence and to mutual cancellation of the local vibrational dipole components<sup>3</sup>. The  $^{31}\text{P}$ - $^1\text{H}$  NMR spectra of  $\text{CD}_2\text{Cl}_2$  solutions of **(2A)**–**(2D)** show one broad signal. FAB-mass spectra show fragmentation *via* successive loss of CO and fragmentation of the organic ligands. The IR spectra data in KBr for **(3A)**–**(3D)** show five bands. The selection rules require seven CO modes in the spectrum. Five of them are clearly present. The  $^{31}\text{P}$ - $^1\text{H}$  NMR spectra of  $\text{CD}_2\text{Cl}_2$  solutions of **(3A)**–**(3D)** show one signal. Mass spectra show fragmentation *via* successive loss of CO and fragmentation of the organic ligands.

### **ACKNOWLEDGEMENTS**

We thank TÜBİTAK and the Research Foundation of Ege University for funds and the University of Bristol for allocation of time at the NMR and mass spectrometer.

### **REFERENCES**

1. L. Marko, G. Bor, E. Klumpp, B. Marko and G. Almasy, *Chem. Ber.*, **96**, 55, (1963).
2. G. Natile, S. Pignataro, G. Innorta and G. Bor, *J. Organomet Chem.*, **40**, 955, (1972).
3. G. Geravasio, F. Musso, S. Vastag, G. Bor, G. Szalontai and L. Marko, *J. Cluster Science*, **5**, 401, (1994).
4. K. Baker and G. W. A. Fowles, *J. Less Common Met.*, **8**, 45, (1965).
5. H. Teichmann, *Angew. Chem., Int. Ed. Engl.*, **4**, 785, (1965).
6. D. W. Meek, and P. J. Nicpon, *J. Am. Chem. Soc.*, **87**, 4951, (1965).
7. M. J. Almond, F. Sarikahya, and O. S. Şentürk, *Polyhedron*, **16**, 1101, (1997).
8. F. Sarikahya and O. S. Şentürk, *Synth. and React. in Inorg. Met.-Org. Chem.*, (1999), submitted.
9. R. A. J. O'Hair, J. C. Sheldon and H. H. Bowie, *J. Chem. Soc., Dalton Trans.*, 2837, (1988).
10. M. J. Almond, M. G. B. Drew, F. Sarikahya, and O. S. Şentürk, *Polyhedron*, **14**, 1433, (1995).
11. T. Moeller, H. J. Birch and N. C. Nielson, *Inorg. Synth.*, **4**, 71, (1953); S. A. Butter and J. Chatt, *J. Inorg. Synth.*, **15**, 186, (1974); A. I. Vogel, "Textbook of Practical Organic Chemistry, 3rd Edn., Longman, London, pp. 139-145, 163-179, 193 and 280-288, (1977); H. Nierbergall, and B. Langenfeld, *Chem. Ber.*, **95**, 64, (1962).
12. P. J. Christen, L. M. Van derLinde and F. N. Hooge, *Rec. Trav. Chim.*, **78**, 161, (1959).

Received: 25 August 1999

Referee I: K. Moedritzer

Accepted: 16 June 2000

Referee II: Y. Tor