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Reactions of sulfido-tricobalt cluster $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-C,N-}C_5H_4N)$ with diphosphine ligands and $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-S,P-SPMe}_2)$ towards diphenyl-2-pyridylphosphine

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Abstract

Reaction of sulfido-tricobalt cluster, $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-S,P-SPMe}_2)$ (**8**), with PPh_2py in THF at 90 °C for 6 h gave two compounds, $(\mu_3\text{-S})Co_3(CO)_5(\mu\text{-S,P-SPMe}_2)(\mu\text{-P,N-PPh}_2py)$ (**9**) and $(\mu_3\text{-S})Co_3(CO)_4(\mu\text{-S,P-SPMe}_2)(\mu\text{-P,N-PPh}_2py)(PPh_2py)$ (**10**). Both compounds, **9** and **10**, were well characterized by spectroscopic means as well as X-ray crystal structure determination. The hybrid bidentate PPh_2py ligand bridges two cobalt centers in **9** (or **10**) through both phosphorus and nitrogen atoms. Besides the bridging PPh_2py ligand, one more additional coordinating PPh_2py ligand attached through phosphorous was observed at **10**. Treatment of another sulfido-tricobalt cluster $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-C,N-}C_5H_4N)$ (**2a**) with bis(diphenylphosphino)methane (DPPM) in THF at 25 °C for 2 h gave two DPPM bridged complexes $(\mu_3\text{-S})Co_3(CO)_5(\mu\text{-C,N-}C_5H_4N)(\mu\text{-P,P}'\text{-DPPM})]$ (**11**) and $(\mu_3\text{-S})Co_3(CO)_5[(\mu\text{-C}(=O)\text{,N-}C_5H_4N(C=O))(\mu\text{-P,P}'\text{-DPPM})]$ (**12**) where as bis(diphenylphosphino)ethane (DPPE) gave two DPPE bridged isomeric complexes $(\mu_3\text{-S})Co_3(CO)_5[(\mu\text{-C}(=O)\text{,N-}C_5H_4N(C=O))(\mu\text{-P,P}'\text{-DPPE})]$ (**13a** and **13b**). The X-ray structural analyses of **12** and **13b** revealed that carbonylation occurred at the Co–C(pyridyl) bond.

Keywords: Carbonylation; Sulfido-tricobalt cluster; DPPM; DPPE; Diphenyl-2-pyridylphosphine

1. Introduction

The paramagnetic sulfido-tricobalt carbonyl $(\mu_3\text{-S})Co_3(CO)_9$ is a rather common building unit in cobalt–sulfur clusters [1]. One of the most frequently employed working methods to eradicate the paramagnetic nature of the clusters is to prepare clusters with the general formula $(\mu_3\text{-S})Co_3(CO)_7(\mu\text{-X})$ (X: a bridging, three-electron donating ligand) [2].

In this regards we had previously demonstrated that the pyridyl derivatives shows excellent bridging three-electron donating ligands [3]. Several sulfido-tricobalt clusters as well as tris-mercaptopyridyl chelated mono-cobalt complexes were prepared from the reactions of a variety of mercaptopyridines with $Co_2(CO)_8$ (Scheme 1). An unusual carbonylation was found to take place at the Co–C(pyridyl) bond of the sulfido-tricobalt carbonyl cluster while reacting with external ligands such as carbon monoxide or diphenyl-2-pyridylphosphine.

Meanwhile, using pyridylphosphine as a multi-dentate ligand on the coordination of transition metals has recently attracted much attention [4]. The reaction mechanism for the formation of diphenyl-2-pyridylphosphine bridged sulfido-tricobalt cluster **6** from **2** is proposed as follows (Scheme 2). First, the phosphorous atom of the PPh_2py ligand coordinates to the non-bridged cobalt atom of **2** and replaces one of the three CO ligands. It is then followed by the attack of the pyridyl nitrogen to the adjoining cobalt atom which contains a Co–C(pyridyl) bond, rather than the Co–N(pyridyl) bond. One of the two terminal COs was

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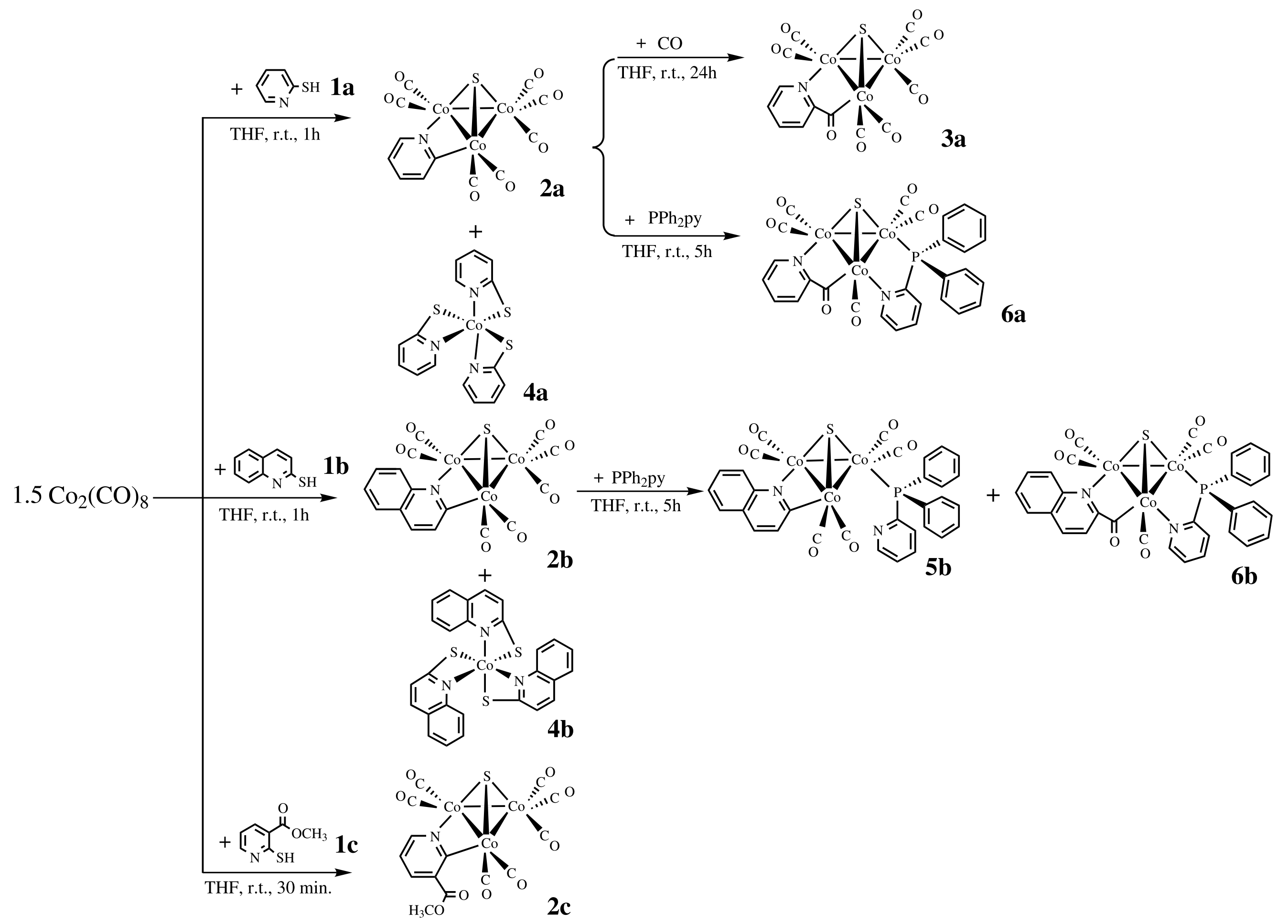
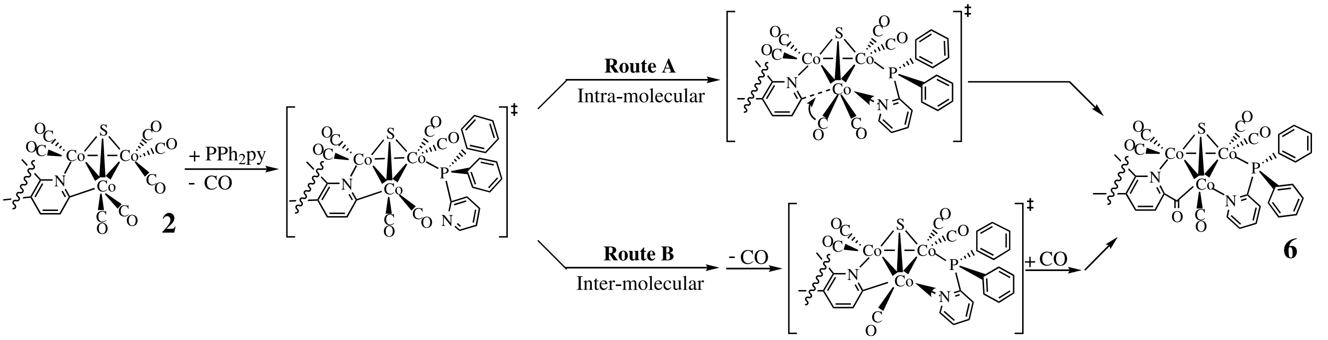


Scheme 1.

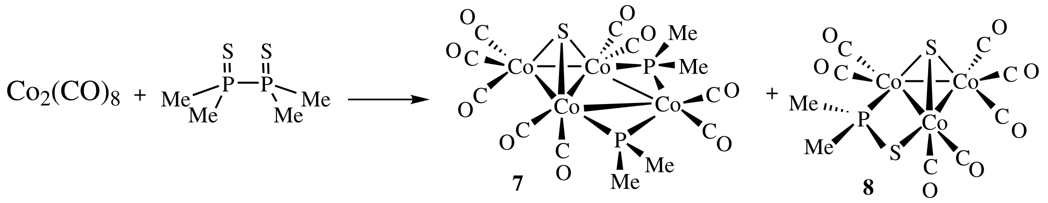
extruded from this specific cobalt center. Then, it may either undergo a concerted, intra-molecular pathway or a stepwise, inter-molecular route while forming **6**.

The preparation of another type of diamagnetic sulfido-tricobalt cluster, (μ_3-S)$Co_3(CO)_7$(μ-S,P-$SPMe_2$) (**8**), was illustrated elsewhere [5] (Scheme 3). The sulfido-tricobalt cluster is bridged by a three-electron donating ligand, μ-S,P-$SPMe_2$. Unfortunately, the crystal data of **8** was not available due to its oily nature during crystallization.

We are interested in probing the cause behind the carbonylation that takes place at the sulfido-tricobalt carbonyl cluster while reacting with external ligands such as PPh_2py and diphosphine ligands. Herein we report some notable results from the reactions between the sulfido-tricobalt cluster (μ_3-S)$Co_3(CO)_7$(μ-C,N-C_5H_4N) (**2a**) with diphosphine ligands such as DPPM and bis(diphenylphosphino)ethane (DPPE) and also from the reaction of (μ_3-S)$Co_3(CO)_7$(μ-S,P-$SPMe_2$) (**8**) towards diphenyl-2-pyridylphosphine.



Scheme 2. Proposed reaction mechanism for the formation of **6**.



Scheme 3.

2. Results and discussion

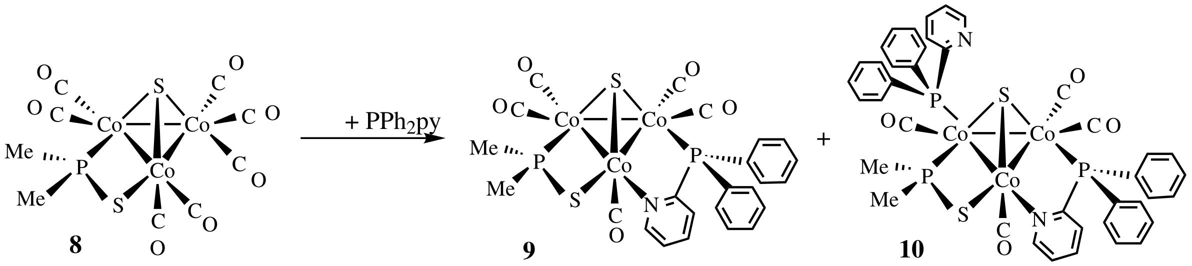
2.1. Reaction of (μ_3-S)$Co_3(CO)_7$(μ-S,P-$SPMe_2$) (**8**) with diphenyl-2-pyridylphosphine

Reaction of sulfido-tricobalt cluster, (μ_3-S)$Co_3(CO)_7$(μ-S,P-$SPMe_2$) (**8**), with PPh_2py in THF at 90 °C for 6 h gave two compounds, (μ_3-S)$Co_3(CO)_5$(μ-S,P-$SPMe_2$)(μ-P,N-PPh_2py) (**9**) and (μ_3-S)$Co_3(CO)_4$(μ-S,P-$SPMe_2$)(μ-P,N-PPh_2py)(PPh_2py) (**10**) (Scheme 4).

Compounds, **9** and **10**, were well characterized by spectroscopic means. Both ^{1}H- and ^{13}C-NMR data revealed that two methyl groups on **9** (or **10**) are not chemical equivalent. A distinct down-fielded doublet signal in ^{1}H-NMR of **9** (or **10**) was assigned to the nitrogen-neighboring proton of the coordinated pyridyl. It indicates that the diphenyl-2-pyridylphosphine acts as a bridging ligand. It is always difficult to observe the carbonyl peaks from ^{13}C-NMR for the sulfido-tricobalt carbonyl clusters as it is the case here. Crystals of **9** and **10** were obtained from the CH_2Cl_2 solution under 4 °C and the structures were determined (Table 1). Solvent molecules, CH_2Cl_2 and toluene, were found to be intercalated between the spaces of the packed molecules of **10**. The molecular structures of **9** and **10** reveal that reactant **8** is either bridged by one PPh_2py ligand in forming **9** or together bridged and coordinated by two PPh_2py ligands in forming **10** (Figs. 1 and 2). It is believed that the formation of **9** or **10** was through a similar, yet slightly different, reaction route as shown in Scheme 4. The first coordination of the PPh_2py ligand is presumably through the phosphorous of **9** (or **10**) to the less crowded cobalt atom, a cobalt center with three CO ligands, and replacing one of them. It is then followed by the attack of the pyridyl nitrogen to the adjoining cobalt atom which contains a Co–S(Me_2PS) bond. It comes naturally for the second coordinating PPh_2py ligand to take the position of a less crowded region, which is away from the existed PPh_2py ligand, and resulted in the formation of **10**. The anticipated carbonylation did not take place at the Co–S(Me_2PS) bond of the sulfido-tricobalt carbonyl cluster in this case. It is believed that the formation of a Co–C(=O)–S(Me_2PS) bond by CO insertion into the Co–S(Me_2PS) bond is much difficult than the formation of a Co–C(=O)–C(pyridyl) bond by CO insertion into the Co–C(pyridyl) bond. It is probably due to the fact that two elements, sulfur and carbon atoms, belong to two different rows and will bring about weaker bonding for the former than the latter case [6]. The four atoms P, S, Co(1), and Co(3) of **9** and P, S, Co(1), and Co(2) of **10** are almost coplanar and with a trapezoid form. Yet, the phosphorus and nitrogen atoms of the bridging PPh_2py and the two PPh_2py-bridged cobalt atoms are not coplanar for both cases. The bridging μ-P,N-PPh_2py and μ-S,P-$SPMe_2$ as well as the coordinating PPh_2py ligand all take the equatorial positions of the clusters. The bond lengths of the three Co–S bonds are more or less equal and the non-ligand-bridged Co–Co bond length is the longest among all three cobalt–cobalt bonds for both cases as expected.

2.2. Reaction of (μ_3-S)$Co_3(CO)_7$(μ-C,N-C_5H_4N) (**2a**) with bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane

Treatment of sulfido-tricobalt cluster (μ_3-S)$Co_3(CO)_7$(μ-C,N-C_5H_4N) (**2a**) with bis(diphenylphosphino)methane (DPPM) in THF at 25 °C for 2 h gave two DPPM bridged complexes (μ_3-S)$Co_3(CO)_5$(μ-C,N-C_5H_4N)(μ-P,P′-DPPM)] (**11**), (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N-C_5H_4N(C=O))(μ-P,P′-DPPM)] (**12**). Similar reac-



Scheme 4.

Table 1
Crystal data of **9**, **10**, **12** and **13b**

Compound	**9**	**10**	**12**	**13b**
Formula	$C_{24}H_{20}Co_3NO_5P_2S_2$	$C_{40}H_{34}Co_3N_2O_4P_3S_2\cdot CH_2Cl_2\cdot C_7H_8$	$C_{36}H_{24}Co_3NOP_2S\cdot CH_2Cl_2$	$C_{37}H_{28}Co_3NO_6P_2S$
Formula weight	705.26	1117.51	924.28	853.39
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	15.0063(9)	10.9566(9)	10.7166(8)	10.1251(8)
b (Å)	12.1967(7)	12.7493(11)	11.4931(8)	15.6767(13)
c (Å)	16.0407(10)	19.2481(16)	17.0001(13)	23.1129(18)
α (°)	–	82.516(2)	102.457(2)	–
β (°)	103.5910(10)	75.537(2)	101.057(2)	90.526(2)
γ (°)	–	74.701(2)	90.702(2)	–
V (Å^3)	2853.7(3)	2505.3(4)	2003.5(3)	3668.5(5)
Z	4	2	2	4
D_{calc} (mg m^{-3})	1.640	1.471	1.529	1.545
λ (Mo–K$_\alpha$) (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	2.014	1.311	1.537	1.531
2θ Range (°)	2.12–26.01	1.92–26.02	1.94–26.02	2.01–26.04
Observed reflections ($F > 4\sigma(F)$)	5598	9692	7758	7224
No. of refined parameters	334	577	487	451
R_1 [a] for significant reflections	0.0304	0.0412	0.0447	0.0473
wR_2 [b] for significant reflections	0.1243	0.1363	0.1146	0.1139
GoF [c]	1.168	1.124	0.817	0.767

[a] $R_1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$.

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 0.10$ for **9**, **10**, **12** and **13b**.

[c] $\text{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{\text{rflns}} - N_{\text{params}})]^{1/2}$.

tion was carried out for **2a** with DPPE in THF at 25 °C for 3 h. Two DPPE bridged complexes (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N-C_5H_4N(C=O))(μ-P,P′-DPPE)] (**13b**) and presumably its isomeric form **13a** were observed (Scheme 5).

Both compounds, **12** and **13b**, were characterized by spectroscopic means as well as X-ray crystal structure determination (Table 1). The structures of **12** and **13b** reveal that a carbonylation process occurred at the Co–C(pyridyl) bond of **2a**. The five atoms Co(1), C(6), C(1), N and Co(3) of **13b** and Co(1), C(6), C(1), N and Co(3) of **12** are almost coplanar. The bridging μ-P,P-DPPE and μ-P,P-DPPM all take the equatorial positions of the clusters. In this regard, it is similar as the PPh_2py-bridged of **9** or **10**. The bond lengths of the three Co–S bonds are almost identical and the μ-C(=O),N-C_5H_4N(C=O) bridged Co–Co bond length is the shortest among all three cobalt–cobalt bonds for both cases. Unfortunately, attempts to grow crystals from **11** and **13a** were resulted in failure (Table 2). Tentative structural assignment of these two compounds, based on spectroscopic data, are shown in Scheme 5.

The fact that the bridging pattern of DPPM on **12** (or DPPE on **13a**) is different from the previous case, PPh_2py on **6**, is noteworthy. A reaction mechanism for the formations of **12** and **13a** from **2a** is proposed as

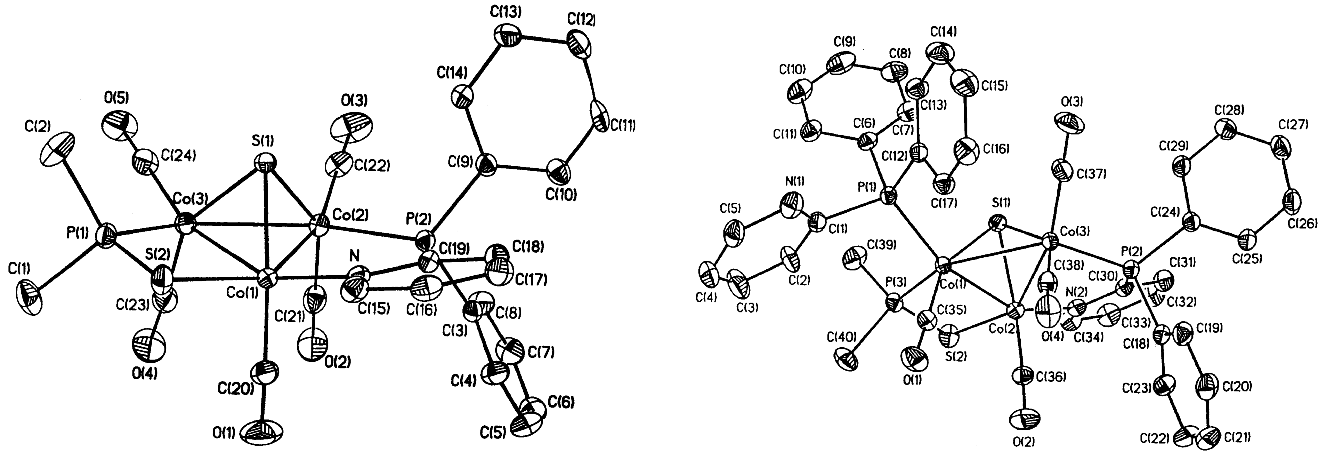


Fig. 1. Molecular structures of (a) (μ_3-S)$Co_3(CO)_5$(μ-S,P-$SPMe_2$)(μ-P,N-PPh_2py) (**9**); (b) (μ_3-S)$Co_3(CO)_4$(μ-S,P-$SPMe_2$)(μ-P,N-PPh_2py)(PPh_2py) (**10**).

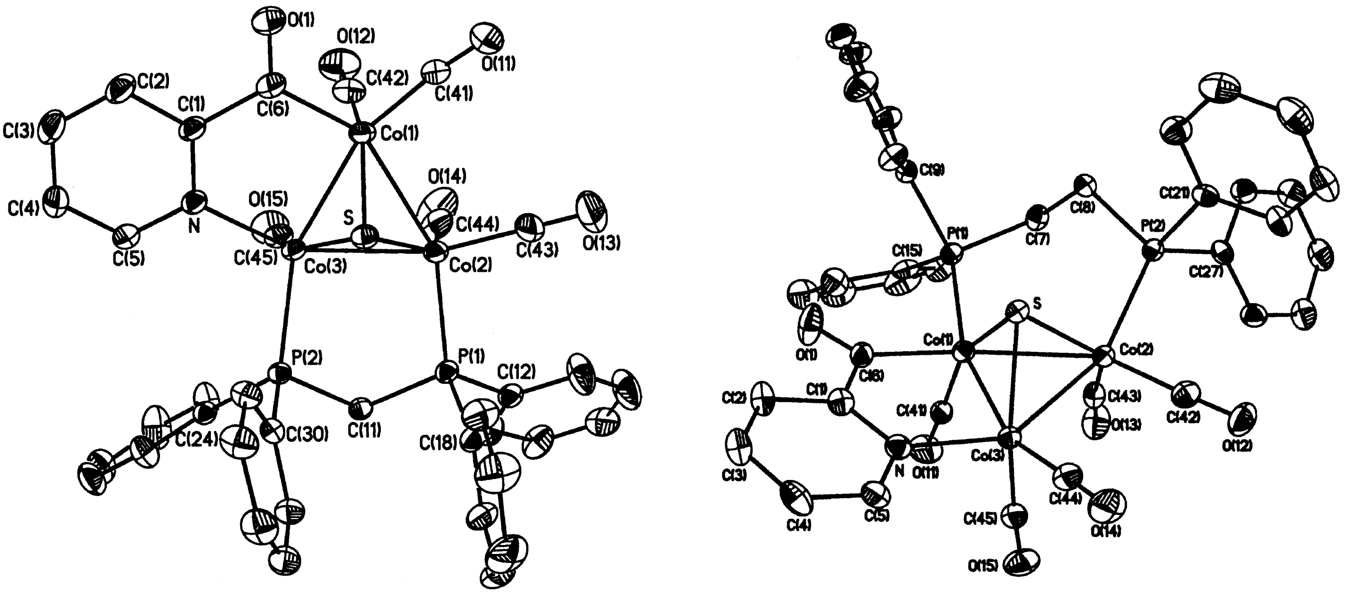
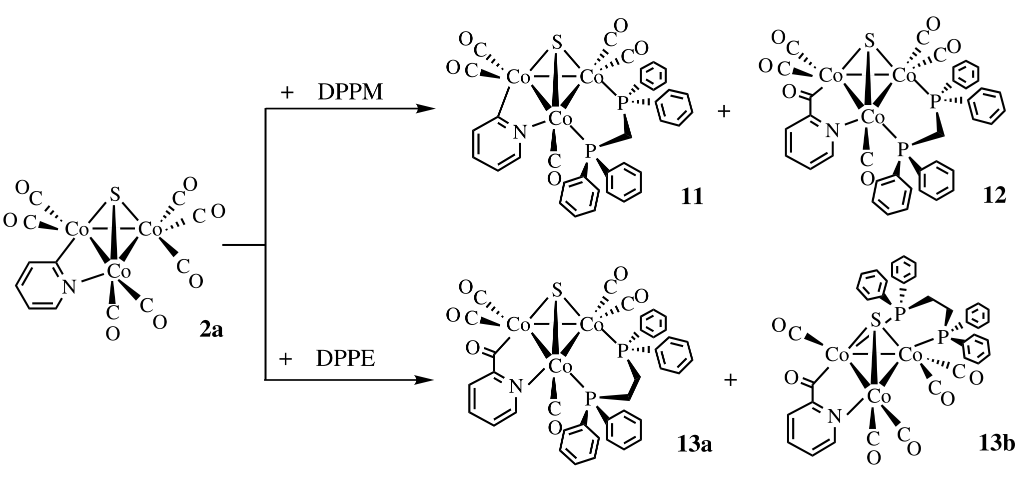


Fig. 2. Molecular structures of (a) (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N-C_5H_4N(C=O))(μ-P,P′-DPPM)] (**12**); (b) (μ_3-S)$Co_3(CO)_5$[(μ-C(=O),N-C_5H_4N(C=O))(μ-P,P′-DPPE)] (**13b**).

shown in Scheme 6. First, the phosphorous of DPPM (or DPPE) ligand coordinates to the non-bridged cobalt atom and replaces one of the CO ligands, then followed by the attack of the other side of phosphorous to the neighboring cobalt atom which either contains a Co–C(pyridyl) or Co–N(pyridyl) bond. In the case of DPPM, it is obvious that the subsequent attack takes place mostly at the Co–N(pyridyl) bond and therefore forms **12**. Nevertheless, the succeeding attack of the other phosphorous of DPPE to the adjoining cobalt atom takes place somewhat evenly both at Co–C(pyridyl) and Co–N(pyridyl) bond and forms both **13a** and **13b**. The differences between two cases might be caused by the formation of a relatively stable five-membered ring, Co(3)–P(2)–C(11)–P(1)–Co(2), in **12** and a relatively unstable six-membered ring, Co(2)–P(2)–C(8)–C(7)–P(1)–Co(1), in **13**. In contrast to the case of **6**, the formation of **12** (or **13a**) can only be achieved through an inter-molecular means. It is, therefore, obvious that the coordinating capacities of these two types of ligands, DPPM and DPPE versus PPh_2py, are not quite the same in terms of the subsequent attack on the second cobalt center. It is believed that the relatively strong hardness of the nitrogen atom on PPh_2py, compared with the phosphorus atom on DPPE (or DPPM), keeps it away from the pyridine coordinated cobalt center during the succeeding attack. In contrast, the phosphorus atom on DPPE (or DPPM) might preferably attack the pyridine coordinated cobalt center [7].



Scheme 5.

Table 2
Selected bond lengths (Å) and bond angles (°)

Compound ***9***			
Bond lenghts			
Co(1)–S(1)	2.1844(6)	Co(2)–S(1)	2.1590(7)
Co(3)–S(1)	2.1661(7)	Co(1)–Co(2)	2.4799(4)
Co(1)–Co(3)	2.4800(5)	Co(2)–Co(3)	2.5428(5)
Co(2)–P(2)	2.1812(7)	Co(3)–P(1)	2.1947(8)
Co(1)–N	2.004(2)	Co(1)–S(2)	2.3207(7)
S(2)–P(1)	2.0346(10)		
Bond angles			
Co(2)–Co(1)–Co(3)	61.684(13)	Co(1)–Co(2)–Co(3)	59.161(13)
Co(1)–Co(3)–Co(2)	59.155(13)	Co(2)–S(1)–Co(3)	72.02(2)
Co(2)–S(1)–Co(1)	69.63(2)	Co(3)–S(1)–Co(1)	69.51(2)
S(1)–Co(3)–Co(1)	55.595(19)	S(1)–Co(3)–Co(2)	53.860(19)
S(1)–Co(2)–Co(3)	54.120(19)	S(1)–Co(2)–Co(1)	55.668(18)
S(1)–Co(1)–Co(2)	54.701(18)	S(1)–Co(1)–Co(3)	54.898(19)
N–Co(1)–Co(2)	100.92(6)	S(2)–Co(1)–Co(3)	89.27(2)
P(1)–S(2)–Co(1)	85.99(3)	S(2)–P(1)–Co(3)	105.81(3)
N–C(19)–P(2)	116.15(17)		
Compound ***10***			
Bond lenghts			
Co(1)–Co(2)	2.4674(5)	Co(1)–Co(3)	2.5701(5)
Co(2)–Co(3)	2.4992(6)	Co(1)–S(1)	2.1712(8)
Co(2)–S(1)	2.1877(9)	Co(3)–S(1)	2.1694(8)
Co(1)–P(3)	2.1978(9)	Co(1)–P(1)	2.2224(8)
Co(3)–P(2)	2.1982(8)	S(2)–P(3)	2.0454(13)
Co(2)–N(2)	2.010(2)	Co(2)–S(2)	2.3190(10)
Bond angles			
Co(1)–Co(2)–Co(3)	62.323(15)	Co(2)–Co(3)–Co(1)	58.234(15)
Co(2)–Co(1)–Co(3)	59.444(15)	S(1)–Co(2)–Co(1)	55.21(2)
S(1)–Co(2)–Co(3)	54.66(2)	S(1)–Co(3)–Co(2)	55.34(2)
S(1)–Co(3)–Co(1)	53.73(2)	S(1)–Co(1)–Co(2)	55.84(2)
S(1)–Co(1)–Co(3)	53.66(2)	S(2)–Co(2)–Co(3)	148.08(3)
S(2)–Co(2)–Co(1)	89.48(3)	Co(3)–S(1)–Co(1)	72.61(3)
Co(3)–S(1)–Co(2)	70.00(3)	Co(1)–S(1)–Co(2)	68.95(3)
N(1)–C(1)–P(1)	123.9(3)	N(2)–C(30)–P(2)	114.3(2)
P(3)–S(2)–Co(2)	85.99(4)	S(2)–P(3)–Co(1)	105.14(4)
Compound ***12***			
Bond lenghts			
Co(1)–C(6)	1.917(5)	Co(1)–S	2.1486(11)
Co(1)–Co(3)	2.4471(7)	Co(1)–Co(2)	2.5261(7)
Co(2)–S	2.1755(11)	Co(2)–P(1)	2.2031(11)
Co(2)–Co(3)	2.5472(8)	Co(3)–N	2.011(3)
Co(3)–S	2.1586(11)	Co(3)–P(2)	2.2324(10)
C(1)–C(6)	1.521(6)	N–C(5)	1.339(5)
N–C(1)	1.349(5)	P(1)–C(11)	1.826(4)
P(2)–C(11)	1.845(4)		
Bond angles			
C(6)–Co(1)–Co(3)	91.10(13)	Co(3)–Co(1)–Co(2)	61.59(2)
P(1)–Co(2)–Co(3)	96.41(3)	Co(1)–Co(2)–Co(3)	57.68(2)
N–Co(3)–P(2)	108.54(9)	N–Co(3)–Co(1)	89.41(9)
P(2)–Co(3)–Co(2)	95.67(3)	Co(1)–Co(3)–Co(2)	60.73(2)
Co(1)–S–Co(3)	69.24(4)	Co(1)–S–Co(2)	71.49(4)
Co(3)–S–Co(2)	71.99(4)	C(11)–P(1)–Co(2)	110.03(12)
C(11)–P(2)–Co(3)	106.99(12)	C(1)–N–Co(3)	120.9(3)
N–C(1)–C(6)	118.7(3)	C(1)–C(6)–Co(1)	119.2(3)
P(1)–C(11)–P(2)	110.93(18)		
Compound ***13b***			
Bond lenghts			
Co(1)–C(6)	1.911(6)	Co(1)–S	2.1557(16)
Co(1)–P(1)	2.2223(17)	Co(1)–Co(3)	2.4579(10)
Co(1)–Co(2)	2.5643(11)	Co(2)–S	2.1806(16)
Co(2)–P(2)	2.1882(17)	Co(2)–Co(3)	2.5299(11)
Co(3)–N	1.986(5)	Co(3)–S	2.1743(16)
P(1)–C(7)	1.834(6)	P(2)–C(8)	1.819(6)
N–C(1)	1.356(7)	C(1)–C(6)	1.493(8)
C(7)–C(8)	1.538(8)		
Bond angles			
C(6)–Co(1)–P(1)	97.77(19)	C(6)–Co(1)–Co(3)	90.60(19)
P(1)–Co(1)–Co(2)	104.48(5)	Co(3)–Co(1)–Co(2)	60.45(3)
P(2)–Co(2)–Co(1)	109.17(5)	Co(3)–Co(2)–Co(1)	57.69(3)
N–Co(3)–Co(1)	89.43(14)	Co(1)–Co(3)–Co(2)	61.86(3)
Co(1)–S–Co(3)	69.17(5)	Co(1)–S–Co(2)	72.50(5)
Co(3)–S–Co(2)	71.03(5)	C(7)–P(1)–Co(1)	112.6(2)
C(8)–P(2)–Co(2)	113.4(2)	C(8)–C(7)–P(1)	113.5(4)
C(7)–C(8)–P(2)	114.1(4)		

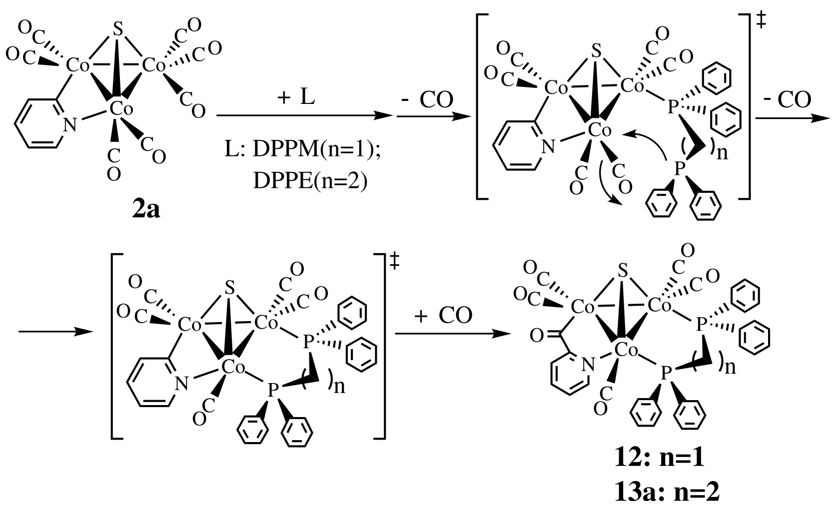
3. Summary

Two classes of sulfido-tricobalt clusters, $(\mu_3\text{-S})\text{Co}_3(\text{CO})_7(\mu\text{-C,N-C}_5\text{H}_4\text{N})$ (**2a**) and $(\mu_3\text{-S})\text{Co}_3(\text{CO})_7(\mu\text{-S,P-SPMe}_2)$ (**8**), were prepared and their reactions towards diphosphine ligands, DPPM and DPPE, and towards diphenyl-2-pyridylphosphine ligand, respectively, were carried out. Carbonylation process only occurs at the Co–C(pyridyl) bond of the former cluster, $(\mu_3\text{-S})\text{Co}_3(\text{CO})_7(\mu\text{-C,N-C}_5\text{H}_4\text{N})$, while it is bridged by either DPPM or DPPE. There is no carbonylation being observed for the latter cluster, $(\mu_3\text{-S})\text{Co}_3(\text{CO})_7(\mu\text{-S,P-SPMe}_2)$, while it is bridged or coordinated by diphenyl-2-pyridylphosphine ligand.

4. Experimental

4.1. General

All operations were performed in a nitrogen flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separations of the products were performed by centrifugal thin layer chromatography (CTLC, Chromatotron, Harrison model 8924). ^{1}H-NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in parts per million relative to internal TMS. ^{31}P- and ^{13}C-NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. Some other ^{1}H-NMR spectra were recorded at Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. IR spectra of sample powder in KBr were recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on Heraeus CHN-O-S-Rapid. Accurate mass and elemental analyses were precluded for some of the following compounds probably due to their chemical labilities.



Scheme 6. Proposed inter-molecular mechanism for the formations of **12** and **13a**.

*4.1.1. The reaction of (μ_3-S)$Co_3(CO)_7$(μ-S,P-$SPMe_2$) (**8**) with diphenyl-2-pyridylphosphine ligand*

The preparative procedure of forming **8** was described by Natile et al. [8]. Compound **8** was first separated and purified then the reaction of it with diphenyl-2-pyridylphosphine followed.

Into a 100 cm^3 flask was placed **8**, (1.67 g, 4.33 mmol), with one equivalent of diphenyl-2-pyridylphosphine with 20 cm^3 of THF. The solution was stirred at 90 °C for 6 h.

Subsequently, the resulting dark green solution was filtered through a small amount of silica gel. The filtrate was evaporated under reduced pressure to yield the crude product. Purification with centrifugal thin-layer chromatography was carried out with mixture solvent, CH_2Cl_2–hexanes = 1:1. The first dark green band was eluted out and was characterized as (μ_3-S)$Co_3(CO)_5$(μ-S,P-$SPMe_2$)(μ-P,N-PPh_2py) (**9**) with 33% yield. The second dark green band was identified as (μ_3-S)$Co_3(CO)_4$(μ-S,P-$SPMe_2$)(μ-P,N-PPh_2py)(PPh_2py) (**10**) with 26% yield.

*4.1.1.1. Complex **9**.* ^{1}H-NMR($CDCl_3$, δ ppm): 8.17 (d, $J_{H-H} = 5.1$ Hz, 1H, pyridine), 7.46–7.95 (m, 10H, arene), 7.14 (t, 1H, pyridine), 7.03 (m, 1H, pyridine), 6.66 (d, $J_{H-H} = 7.5$ Hz, 1H, pyridine), 2.01 (d, $J = 9.6$ Hz, 3H, CH_3), 1.536 (d, $J = 9.3$ Hz, 3H, CH_3); ^{13}C-NMR ($CDCl_3$): 149.63 (d, $J = 9.0$ Hz, 1C, pyridine), 136.42 (d, $J = 5.2$ Hz, 1C, ipso of arene), 135.59 (d, 1C, pyridine), 134.17 (d, $J = 9.8$ Hz, 1C, ipso of arene), 133.42 (d, 1C, pyridine), 132.39 (d, $J = 5.2$ Hz, 2C, arene), 131.49 (s, 2C, arene), 128.87 (d, 2C, arene), 128.30 (d, $J = 6.0$ Hz, 2C, arene),124.88 (s, 1C, pyridine), 27.41 (1C, CH_3), 25.89 (1C, CH_3); ^{31}P-NMR ($CDCl_3$): 28.0, 38.0; E.A.: Calc. C: 40.85, H: 2.84; Found: C, 41.15, H, 2.73%; IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)} = 1991$(m), 2037(sh); MS (FAB): 706 [$M^+ + 1$].

*4.1.1.2. Complex **10**.* ^{1}H-NMR ($CDCl_3$, δ ppm): 6.46 (d, $J_{H-H} = 7.4$ Hz, 1H, pyridine), 7.02 (d, 1H, pyridine), 7.89 (d, 1H, pyridine), 8.09 (d, $J_{H-H} = 7.5$ Hz, 1H, pyridine), 8.74 (d, 1H, pyridine), 7.36–7.43 (m, 10H, arene), 1.36 (d, $J = 8.0$ Hz, 3H, CH_3), 1.57 (d, $J = 7.8$ Hz, 3H, CH_3); ^{13}C-NMR ($CDCl_3$): 153.88 (d, 1C, pyridine), 149.77 (m, 1C, pyridine), 135.51 (s, 1C, pyridine), 134.78 (s, 1C, pyridine), 134.08 (d, 2C, ipso of arene), 132.45 (d, 2C, ipso of arene), 133.23 (dd, 4C, arene), 131.33 (dd, 4C, arene), 127.93–129.73 (12C, arene), 124.77 (s, 1C, pyridine), 123.00 (s, 1C, pyridine), 29.29 (1C, CH_3), 24.75 (1C, CH_3); ^{31}P-NMR ($CDCl_3$): −3.0, 21.9, 38.4; E.A.: Calc. C: 51.06, H: 3.62; Found: C, 54.63; H, 4.87%; IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)} =$ 1890(w), 1933(w), 1970(s), 2003(m), 2054(sh).

*4.1.2. The reactions of (μ_3-S)$Co_3(CO)_7$(μ-C,N-C_5H_4N) (**2a**) with bis(diphenylphosphino)methane and bis(diphenylphosphino)ethane*

Into a 100 cm^3 flask was placed **2a** (0.297 g, 0.620 mmol) with DPPM (0.230 g, 0.620 mmol) in 20 cm^3 THF with a N_2 balloon. The solution was stirred at 25 °C for 2 h. Subsequently, the solvent of the resulting brown solution was removed and the residue was chromatographed by CTLC in a CH_2Cl_2–hexane = 1:1 mixed solvent. The first band, brown in color of **11** (0.1036 g, 0.1277 mmol), was obtained. The yield is 21%. The identity of the second band, red in color with rather small amount, is not known. The third green band of **12** (0.1990 g, 0.2371 mmol) with 39% yield was separated out.

Following the same processes, compound **2a** (0.320 g, 0.670 mmol) with molar equivalent of DPPE (0.266 g, 0.670 mmol) were dissolved in 20 cm^3 THF, then was transferred into a 100 cm^3 flask with a jointed balloon. The solution was stirred at 25 °C for 3 h. Subsequently, the solvent of the resulting brown solution was removed and the residue was chromatographed by CTLC in a CH_2Cl_2–hexane = 1:1 mixed solvent. The first band, brown in color of **13a** (0.244 g, 0.276 mmol), was obtained. The yield is 41%. The second pale green band of **13b** (0.194 g, 0.219 mmol) with 29% yield was separated out. The identity of the third band, red in color with rather small amount, is not known.

*4.1.2.1. Complex **11**.* ^{1}H-NMR ($CDCl_3$, δ ppm): 6.28 (t, $J_{H-H} = 5.7$ Hz, 1H, pyridine), 6.80 (t, $J_{H-H} = 7.2$ Hz, 1H, pyridine), 7.11 (d, $J_{H-H} = 5.1$ Hz, 1H, pyridine), 7.23–7.75 (m, 20H, arene, 1H, pyridine), 3.07 (m, 1H, CH_2), 3.39 (m, 1H, CH_2); ^{13}C-NMR ($CDCl_3$): 153.20 (s, 1C, pyridine), 119.09–137.31 (m, 20C, arene, 3C, pyridine), 44.04 (t, 1C, CH_2); ^{31}P-NMR ($CDCl_3$): 25.27, 36.68; E.A.: Calc. C: 51.81; H, 3.23; Found: C, 49.41; H, 5.59%; IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)} = 1982$, 2024.

*4.1.2.2. Complex **12**.* ^{1}H-NMR ($CDCl_3$, δ ppm): 6.43 (t, $J_{H-H} = 5.9$ Hz, 1H, pyridine), 6.89 (d, $J_{H-H} = 7.5$ Hz, 1H, pyridine), 7.07–7.61 (m, 20H, arene, 2H, pyridine), 2.69 (m, 1H, CH_2), 3.45 (m, 1H, CH_2); ^{13}C-NMR ($CDCl_3$): 162.90 (s, 1C, pyridine), 154.46 (s, 1C, pyridine), 116.23–137.09 (m, 20C, arene, 3C, pyridine), 42.84 (t, 1C, CH_2); ^{31}P-NMR ($CDCl_3$): 34.22, 40.80; E.A.: Calc. C: 51.51%; H, 3.12%. Found: C, 50.01%; H, 3.57%; IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)} = 1980$, 2031; m.p. = 160–218 °C (dec.)

*4.1.2.3. Complex **13a**.* ^{1}H-NMR ($CDCl_3$, δ ppm): 7.29–7.77 (m, 20H, arene, 1H, pyridine) 7.05 (1H, pyridine), 6.78 (1H, pyridine), 6.22 (1H, pyridine), 1.8–2.2 (m, 4H, DPPE); ^{13}C-NMR ($CDCl_3$): 163.15 (s, 1C, pyridine), 155.04 (s, 1C, pyridine), 153.48 (s, 1C, pyridine), 116.33–137.22 (m, 20C, arene, 2C, pyridine), 25.27 (d, 1C, CH_2), 25.87 (d, 1C, CH_2). E.A.: Calc. C: 52.07; H, 3.31. Found: C, 50.78; H, 3.69%; MS (FAB): 851 [M$^+$ −1].

*4.1.2.4. Complex **13b**.* ^{1}H-NMR ($CDCl_3$, δ ppm): 8.34 (1H, pyridine), 7.04–7.78 (m, 20H, arene, 1H, pyridine), 6.87 (1H, pyridine), 6.76 (1H, pyridine), 1.6–1.8 (m, 4H, DPPE); ^{13}C-NMR ($CDCl_3$): 163.16 (s, 1C, pyridine), 155.07 (s, 1C, pyridine), 126.12–137.36 (m, 20C, arene, 3C, pyridine), 25.82 (d, 1C, CH_2), 24.49 (d, 1C, CH_2); ^{31}P-NMR ($CDCl_3$): 33.08, 48.27; E.A.: Calc. C: 52.90; H, 4.10. Found: C, 52.55; H, 4.59%; IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)} = 1982$(m), 2028; m.p. = 160–170 °C (dec.).

5. X-ray crystallographic studies

Suitable crystals of **9**, **10**, **12** and **13b** were sealed in thin-walled glass capillaries under nitrogen atmosphere and were mounted on a Siemens Smart CCD diffractometer. The crystallographic data were collected using a θ–2θ scan mode with Mo–K_α radiation. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed by the structure solution. The structure was solved by direct methods using Siemens SHELXTL PLUS package [9]. All the non-H atoms were located from successive Fourier maps. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic for H atoms that were refined using riding model [10]. Crystallographic data of **9**, **10**, **12** and **13b** are summarized in Table 1.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 159095 for compound **9**, CCDC no. 159096 for compound **10**, CCDC no. 197042 for compound **12**, CCDC no. 197043 for compound **13b**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) S. Vastag, G. Gerbasio, D. Marabello, G. Szalomtai, L. Markó, Organometallics 17 (1998) 4218;
(b) L. Markó, G. Bor, E. Klumpp, Chem. Ber. 100 (1967) 1451;
(c) E. Klumpp, L. Markó, G. Bor, Chem. Ber. 97 (1964) 926;
(d) S.A. Khattab, L. Markó, G. Bor, B. Markó, J. Organomet. Chem. 1 (1964) 373;
(e) L. Markó, G. Bor, E. Klumpp, B. Markó, G. Almásy, Chem. Ber. 96 (1963) 995;
(f) D.L. Stevenson, V.R. Magnuson, L.F. Dahl, J. Am. Chem. Soc. 89 (1967) 3727;
(g) B. Zhuang, P. Yu, L. Huang, L. He, G. Pan, Polyhedron 16 (1997) 1425;
(h) E.I. Stiefel, K. Matsumoto, Transition Metal Sulfur Chemistry: Biological and Industrial Significance, ACS, Wasghington, DC, 1996.

[2] (a) L. Markó, G. Bor, E. Klumpp, Chem. Ind. (Lond.) (1961) 1491;
(b) C.H. Wei, L.F. Dahl, Inorg. Chem. 6 (1967) 1229;
(c) C.E. Strouse, L.F. Dahl, Discuss. Faraday Soc. 47 (1969) 93;
(d) C.E. Strouse, L.F. Dahl, J. Am. Chem. Soc. 93 (1971) 6032.

[3] F.-E. Hong, S.-C. Chen, Y.-T. Tsai, Y.-C. Chang, J. Organomet. Chem. 655 (2002) 172.

[4] (a) J. Puddephatt, Chem. Soc. Rev. 12 (1983) 99;
(b) J.P. Farr, M.M. Olmstead, N.M. Rutherford, F.E. Wood,

A.L. Balch, Organometallics 2 (1973) 1758;
(c) J.P. Farr, F.E. Wood, A.L. Balch, Inorg. Chem. 22 (1983) 1229;
(d) J.P. Farr, M.M. Olmstead, A.L. Balch, Inorg. Chem. 22 (1983) 3387;
(e) Z.-Z. Zhang, H.K. Wang, H.G. Wang, R.J. Wang, J. Organomet. Chem. 314 (1986) 357;
(f) Z.-Z. Zhang, H.K. Wang, Z. Xi, X.K. Yao, R.J. Wang, J. Organomet. Chem. 376 (1989) 123;
(g) Z.-Z. Zhang, H. Cheng, Coord. Chem. Rev. 147 (1996) 1;
(h) K. Kurtev, D. Ribola, R.A. Jones, D.J. Cole-Hamilton, G. Wilkinson, J. Chem. Soc. Dalton Trans. (1980) 55;
(i) E. Linder, H. Rauleder, P. Wegner, Zeitschrift Für Naturforschung B39 (1984) 1224.

[5] (a) G. Natile, S. Pignataro, G. Innorta, G. Bor, J. Organomet. Chem. 40 (1972) 215;
(b) G. Gervasio, F. Musso, S. Vastag, G. Bor, G. Szalontai, L. Markó, J. Clust. Sci. 5 (1994) 401.

[6] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, second ed. (Chapter 7), Wiley, 1994.

[7] (a) R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533;
(b) R.G. Pearson (Ed.), Hard and Soft Acids and Bases, Dowden, Hutchinson and Ross, Stroudsburg, 1973;
(c) R.G. Pearson, Chemical Hardness, in: K. Sen (Ed.), Struct. Bond., Springer-Uerlag, vol. 80 (1993) 1.

[8] See Ref. [5a].

[9] G.M. Sheldrick, SHELXTL PLUS User's Manual. Revision 4.1 Nicolet XRD Corporation, Madison, Wisconsin, USA, (1991).

[10] Hydrogen atoms were ride on carbons or oxygens in their idealized positions and held fixed with the C–H distances of 0.96 Å.