



# Dithiocarbonato nickel, palladium and platinum complexes bearing bis(diphenylphosphino)ferrocene: synthesis and X-ray structure determination

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**Abstract.** The dithiocarbonato metal complexes  $M(\kappa^2S,S-S_2CO)(\kappa^2P,P-dppf)$  {M= Ni, Pd, Pt; dppf= bis(diphenylphosphino)ferrocene} are obtained from the reaction of the metal(II) complexes  $[M(\kappa^2S,S-S_2COEt)_2]$  with the dppf ligand or from the chloride substitution of  $M(\kappa^2P,P-dppf)Cl_2$  by the *O*-ethylthiocarbonato anion. These complexes are produced by C-O bond cleavage by the *O*-ethylthiocarbonato anion present in solution. These new complexes have been characterized by UV-Vis, NMR, IR spectroscopy and elemental analysis. The structures of the three complexes were further confirmed by single-crystal X-ray diffraction analysis.

**Keywords.** Dithiocarbonate; structure; synthesis; characterization.

## 1. Introduction

*O*-alkyldithiocarbonato ligands, known as xanthates, and their metal complexes have many uses such as metal-ore flotation,<sup>1–4</sup> vulcanization of rubber,<sup>5</sup> biological remediation,<sup>6</sup> non-linear optical applications,<sup>7</sup> synthetic precursors for the generation of metal sulfide nanoparticles,<sup>8,9</sup> as well as their investigation for possible use as therapeutic agents.<sup>10–13</sup> The complex bis(*O*-ethylthiocarbonato)platinum(II), named thioplatin, is found to have antitumor activity against a number of human tumor lines.<sup>13</sup> Its antitumor activity on some human tumors was comparable to cisplatin, but with a significantly lower toxicity on kidneys, small intestines and white blood cells.<sup>14</sup>

Analogous complexes to thioplatin, of the formula  $[Pt(\kappa^2S,S-S_2COR)_2]$  containing different alkyl groups, were synthesized and their cytotoxic activity was tested against several human tumor lines.<sup>11,12</sup> Complexes with short *n*-alkyl chains were found to display significantly higher activity than those with long chains. Complexes

derived from secondary xanthates are also more active than those derived from primary ones.<sup>11,12</sup>

The reactions of nickel, palladium or platinum salts with the *O*-alkyldithiocarbonato anions produced the bis(*O*-alkyldithiocarbonato)metal(II) complexes in fairly high yields.<sup>14–19</sup> The reaction of  $[Ni(\kappa^2S,S-S_2COR)_2]$  with excess triphenylphosphine produced the dithiocarbonato complex  $[Ni(\kappa^2S,S-S_2CO)(PPh_3)_2]$ .<sup>20,21</sup> The corresponding reaction with  $PMePh_2$  gave a six-coordinate complex  $[Ni(\kappa^2S,S-S_2COEt)_2(PMePh_2)_2]$  with two chelated alkyldithiocarbonato ligands for the ethyl complex and a tetracoordinate one  $[Ni(\kappa^2S,S-S_2COC_6H_{11})(\kappa^1S-S_2COC_6H_{11})(PMePh_2)]$  with one bidentate and one monodentate alkyldithiocarbonato ligands for the cyclohexyl derivative.<sup>22</sup> The strong chelate ligand bis(diphenylphosphino)ethane (dppe) reacted with  $[Ni(\kappa^2S,S-S_2COEt)_2]$  forming an equilibrium mixture of five-coordinate complex  $[Ni(\kappa^2S,S-S_2COEt)(\kappa^1S-S_2COEt)(\kappa^2P,P-dppe)]$  and a six-coordinate one  $[Ni(\kappa^2S,S-S_2COEt)_2(\kappa^2P,P-dppe)]$ . However, the cyclohexyl derivative reacted with excess dppe forming the dithiocarbonato complex  $Ni(\kappa^2S,S-S_2CO)(\kappa^2P,P-dppe)$ .<sup>23,24</sup> In another study, the complexes  $[Ni(\kappa^2S,S-S_2COR)_2]$  (R= Me, Et) reacted with dppe to produce products depending on the reaction's conditions.

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The 1:2 metal to ligand ratio-reaction gave the trimer  $[\text{Ni}_3(\mu\text{-S})_2(\kappa^2\text{S,S-SCOR})_2(\text{dppe})]$  if the reaction is carried out at room temperature. However, the 1:1 molar ratio-reaction gave the dithiocarbonato complex  $[\text{Ni}(\kappa^2\text{S,S-S}_2\text{CO})(\kappa^2\text{P,P-dppe})]$ .<sup>24</sup> The reaction of  $[(\kappa^2\text{P,P-dippe})\text{NiBr}_2]$  with  $\text{ROCS}_2^-$  (R= Me, Et, Pr) gave the dithiocarbonato complex  $[\text{Ni}(\kappa^2\text{-S,S-S}_2\text{CO})(\kappa^2\text{P,P-dippe})]$ .<sup>25</sup>

The interaction of bis(*O*-alkyldithiocarbonato)platinum(II) with phosphine ligands has been studied by NMR spectroscopy.<sup>26,27</sup> The reaction of  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{COR})_2]$  (R= Et, Pr<sup>*n*</sup>, CH<sub>2</sub>Ph) with PPh<sub>3</sub> occurred by stepwise cleavage of metal-sulfur bonds to generate four-coordinate compounds  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{COR})(\kappa^1\text{S-S}_2\text{COR})(\text{PPh}_3)]$  with unidentate/bidentate dithiocarbonates and  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{COR})(\text{PPh}_3)_2][\text{S}_2\text{COR}]$  with ionic/bidentate coordination of the sulfur ligands. In addition, a further nucleophilic attack can occur in the OR group to give the dithiocarbonato complex  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{CO})(\text{PPh}_3)_2]$ .<sup>27</sup> The interaction of bis(*n*-propyldithiocarbonato)platinum with several bidentate ligands {P-P = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, (dppe), Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm), Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub> (ape), Ph<sub>2</sub>P(S)CH<sub>2</sub>PPh<sub>2</sub>, (dppmS), Ph<sub>2</sub>P(Se)CH<sub>2</sub>PPh<sub>2</sub> (dppmSe)} is reported.<sup>26</sup> When 1:1 molar reaction of  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{COPr}^n)_2]$  with P-P is carried out at room temperature, one *n*-propyldithiocarbonato ligand is often displaced to give  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{COPr}^n)(\kappa^2\text{P,P-P-P})]^+$  which hydrolyzes to give the dithiocarbonato complex  $[\text{Pt}(\kappa^2\text{S,S-S}_2\text{CO})(\kappa^2\text{-P,P-P-P})]$  and the xanthate ester. If the same reaction is carried out at a low temperature, a different mechanism is observed. First, a complex with monodentate bis(phosphine), mono- and bidentate *n*-propyldithiocarbonato is obtained. Then the latter complex lost a propyldithiocarbonato ligand to form a complex with both bis(phosphine) and *n*-propyldithiocarbonato ligands. At low temperature, the hydrolysis reaction is avoided.<sup>27</sup>

In this report, the interaction of the bis(*O*-ethylthiocarbonato)metal complexes (Ni, Pd, Pt) with 1,1'-bis(diphenylphosphino)ferrocene ligand is described. The molecular structures of the generated complexes are determined.

## 2. Experimental

### 2.1 General

Reactions and manipulations were done under atmospheric condition and normal solvents unless stated otherwise. The following chemicals were used as received (Sigma/Aldrich): potassium *O*-ethylthiocarbonato, 1,1'-bis(diphenylphosphino)ferrocene (dppf), nickel(II) bromide, palladium(II) chloride, potassium tetrachloroplatinate. The following solvents are also used as received (Acros): chloroform, dichloromethane, ethanol, hexane, diethyl ether

and tetrahydrofuran. The complexes  $\text{M}(\kappa^2\text{S,S-S}_2\text{COEt})_2$ <sup>12,13,16</sup> and  $\text{M}(\kappa^2\text{P,P-dppf})\text{X}_2$ <sup>28-30</sup> (M= Ni, Pd, Pt) were prepared by literature methods.

Infrared (IR) spectra were recorded on a Bruker alpha FT-IR spectrometer equipped with ATR unit. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-Avance 400 MHz spectrometer. Chemical shift values are given in ppm and are referenced to SiMe<sub>4</sub> or CHCl<sub>3</sub> (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}), external H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P{<sup>1</sup>H} and to K<sub>2</sub>PtCl<sub>4</sub> for <sup>195</sup>Pt{<sup>1</sup>H}-NMR. Elemental analyses were performed by CHNS and O Thermo Scientific 2000 instrument. The UV-Vis data were collected using a Shimadzu instrument.

### 2.2 General Procedure for the Preparation of $\text{M}(\kappa^2\text{S,S-S}_2\text{CO})(\kappa^2\text{P,P-dppf})$

#### Method A

A mixture of  $\text{M}(\kappa^2\text{P,P-dppf})\text{X}_2$  (1.00 mmol) and EtOCS<sub>2</sub>K (0.320 g, 2.00 mmol) in 50 mL of tetrahydrofuran is stirred for one hour at room temperature. The solution's color lightened and a precipitate is formed. The solution is filtered and the volatiles of the filtrate are removed under vacuum. The resulting solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane at 4 °C.

#### Method B

To a chloroform solution (50 mL) of  $\text{M}(\kappa^2\text{S,S-S}_2\text{COEt})_2$  (1.00 mmol), bis(diphenylphosphino)ferrocene (0.554 g, 1.00 mmol) is added. The mixture is stirred at room temperature for one hour. The volatiles were removed under vacuum leaving a brown-orange solid. The solid was extracted by 3 × 5 mL dichloromethane and filtered. The volatiles of the filtrate were removed under vacuum. The resulting solid was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane at 4 °C.

**2.2a**  $\text{Ni}(\kappa^2\text{S,S-S}_2\text{CO})(\kappa^2\text{P,P-(PPh}_2\text{C}_5\text{H}_4)_2\text{Fe})$  (**1**): Yield: 60%. Brown. IR (KBr, cm<sup>-1</sup>): ν(SC=O) 1659. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.20 (bs, 4H, C<sub>5</sub>H<sub>4</sub>), 4.29 (bs, 4H, C<sub>5</sub>H<sub>4</sub>), 7.44 (m, 12H, Ph), 7.70 (m, 8H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 73.43–77.16 Cp, 128.48–135.56 Ph, 193.71 C=O. <sup>31</sup>P{<sup>1</sup>H} NMR (161.5 MHz, CDCl<sub>3</sub>) δ 30.95. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm) 252, 300, 380. Anal. Calc. for C<sub>35</sub>H<sub>28</sub>FeNiOP<sub>2</sub>S<sub>2</sub> (**1**) C, 59.61; H, 4.00; S, 9.09% Found: C, 58.95; H, 3.85; S, 8.47%.

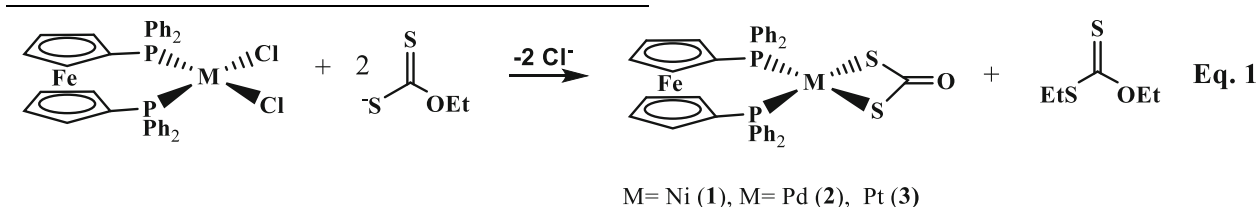
**2.2b**  $\text{Pd}(\kappa^2\text{S,S-S}_2\text{CO})(\kappa^2\text{P,P-(PPh}_2\text{C}_5\text{H}_4)_2\text{Fe})$  (**2**): Yield: 80%. Yellow. IR (KBr, cm<sup>-1</sup>): ν(SC=O) 1678. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.19 (d, 2H, C<sub>5</sub>H<sub>4</sub> *J*<sub>HH</sub>= 4.0 Hz), 4.30 (d, 2H, C<sub>5</sub>H<sub>4</sub> *J*<sub>HH</sub>= 4.0 Hz), 4.39 (d, 2H, C<sub>5</sub>H<sub>4</sub> *J*<sub>HH</sub>= 4.0 Hz), 4.41 (d, 2H, C<sub>5</sub>H<sub>4</sub> *J*<sub>HH</sub>= 4.0 Hz), 7.42 (m, 12H, Ph), 7.78 (m, 8H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 73.25–75.99 Cp, 128.22–135.22 Ph, 197.04 C=O. <sup>31</sup>P{<sup>1</sup>H} NMR (161.5 MHz, CDCl<sub>3</sub>) δ 29.26, 35.53. UV-Vis

(CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm) 252, 304, 378. Anal. Calc. for C<sub>35</sub>H<sub>28</sub>FeOP<sub>2</sub>PdS<sub>2</sub> (**2**) C, 55.83; H, 3.75; S, 8.52%. Found: C, 55.16; H, 3.55; S, 8.36%.

2.2c Pt(κ<sup>2</sup>S,S-S<sub>2</sub>CO)(κ<sup>2</sup>P,P-(PPh<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe) (**3**): Yield: 80%. Orange. IR (KBr, cm<sup>-1</sup>): ν(SC=O) 1685. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.21 (d, 2H, C<sub>5</sub>H<sub>4</sub> J<sub>HH</sub>= 5.0 Hz); 4.22 (d, 2H, C<sub>5</sub>H<sub>4</sub> J<sub>HH</sub>= 5.0 Hz); 4.40 (d, 2H, C<sub>5</sub>H<sub>4</sub> J<sub>HH</sub>= 6.0

Hz); 4.42 (d, 2H, C<sub>5</sub>H<sub>4</sub> J<sub>HH</sub>= 6.0 Hz); 7.33–7.89 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 73.33–75.94 Cp, 128.03–135.15 Ph, 204.52 C=O. <sup>31</sup>P{<sup>1</sup>H} NMR (161.5 MHz, CDCl<sub>3</sub>) δ 12.80 (J<sub>Pt-P</sub>= 3767 Hz), 15.24 (J<sub>Pt-P</sub>= 3242 Hz). <sup>135</sup>Pt{<sup>1</sup>H} NMR (86.0 MHz, CDCl<sub>3</sub>) δ -4379.33 (J<sub>Pt-P</sub>= 3810 Hz). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm) 256, 308, 780. Anal. Calc. for C<sub>35</sub>H<sub>28</sub>FeOP<sub>2</sub>PtS<sub>2</sub> (**3**) C, 49.95; H, 3.35; S, 7.62%. Found: C, 49.34; H, 3.12; S, 6.87%.

on the ethyl carbon resulting into a C-O bond cleavage forming complexes **1–3** and the xanthate ester (Scheme 1). Complexes **1–3** were also obtained from the reactions of M(κ<sup>2</sup>P,P-dppf)Cl<sub>2</sub> with the *O*-ethylthiocarbonyl anion as shown in Equation 1.



Hz); 4.42 (d, 2H, C<sub>5</sub>H<sub>4</sub> J<sub>HH</sub>= 6.0 Hz); 7.33–7.89 (m, 20H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) δ 73.33–75.94 Cp, 128.03–135.15 Ph, 204.52 C=O. <sup>31</sup>P{<sup>1</sup>H} NMR (161.5 MHz, CDCl<sub>3</sub>) δ 12.80 (J<sub>Pt-P</sub>= 3767 Hz), 15.24 (J<sub>Pt-P</sub>= 3242 Hz). <sup>135</sup>Pt{<sup>1</sup>H} NMR (86.0 MHz, CDCl<sub>3</sub>) δ -4379.33 (J<sub>Pt-P</sub>= 3810 Hz). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>, nm) 256, 308, 780. Anal. Calc. for C<sub>35</sub>H<sub>28</sub>FeOP<sub>2</sub>PtS<sub>2</sub> (**3**) C, 49.95; H, 3.35; S, 7.62%. Found: C, 49.34; H, 3.12; S, 6.87%.

### 2.3 X-ray crystal structure analysis

The intensity data for the compounds were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K<sub>α</sub> radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.<sup>31–35</sup>

The structures were solved by direct methods (SHELXS)<sup>34</sup> and refined by full-matrix least squares techniques against Fo<sup>2</sup> (SHELXL-97).<sup>34</sup> All hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All non-disordered, non-hydrogen atoms were refined anisotropically.<sup>34</sup> Crystallographic data, as well as structure solution and refinement details, are summarized in Table 1. XP was used for structure representations.<sup>35</sup>

## 3. Results and Discussion

### 3.1 Synthesis

Treatment of [M(κ<sup>2</sup>S,S-S<sub>2</sub>COEt)<sub>2</sub>] with 1,1'-bis(diphenylphosphino)ferrocene (dppf) gave [M(κ<sup>2</sup>S,S-S<sub>2</sub>CO)(κ<sup>2</sup>P,P-(PPh<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe)] (M= Ni (**1**), Pd (**2**), Pt (**3**)) instead of the expected products [M(κ<sup>2</sup>S,S-S<sub>2</sub>COEt)(κ<sup>2</sup>P,P-(PPh<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe)]<sup>+</sup> (Scheme 1). Complexes **1–3** resulted from the latter cationic complexes by the attack of the dithiocarbonyl anion

Complexes **1–3** have different colors depending on the metal content, the nickel complex is brown, the palladium complex is yellow while the platinum complex is orange. They are soluble in polar organic solvents such as chlorinated solvents, alcohols and insoluble in hydrocarbon solvents and diethyl ether. The complexes were identified based on their IR, <sup>1</sup>H-, <sup>13</sup>C{<sup>1</sup>H}-, <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopy and elemental analysis. The <sup>1</sup>H-NMR spectrum of **1** showed the protons of the cyclopentadienyl ferrocene moiety as two signals at 4.20 and 4.29 ppm which are attributed to α and β protons of the Cp-ring. These bands are shifted to low field compared to those of the (κ<sup>2</sup>P,P-dppf)NiCl<sub>2</sub> (4.02, 4.27 ppm).<sup>16</sup> The same protons of **2** and **3** are shown as four doublets (**2**: 4.19, 4.30, 4.39, 4.41 ppm. **3**: 4.21, 4.22, 4.40, 4.42 ppm) due to possible deviation from coplanarity of the phosphorous atoms relative to their Cp-rings. These ranges are similar to those of (κ<sup>2</sup>P,P-dppf)M(SC<sub>7</sub>H<sub>4</sub>OS)<sub>2</sub> while their splitting is different as the latter complexes showed only two multiplets.<sup>36</sup> The protons of the phenyl groups of the dppf ligand are shown in the spectra as multiplets in the aromatic region with the expected integrations.

Complexes [M(κ<sup>2</sup>S,S-S<sub>2</sub>CO)(κ<sup>2</sup>P,P-(PPh<sub>2</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Fe)] (**1–3**) were also characterized by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy and their spectra showed peaks in the range of 73.43–78.11 ppm for the Cp-rings of ferrocene and peaks in the range of 128.45–135.37 ppm for the phenyl groups. The carbonyl carbon of these complexes are shown as a weak band (**1**: 193.71, **2**: 197.04, **3**: 204.52 ppm). The <sup>195</sup>Pt{<sup>1</sup>H} NMR spectrum of **3** displayed a triplet at -4379.33 ppm with a Pt-P coupling of 3810 Hz. The chemical shift and the coupling constant are within the range observed for phosphine platinum dichalcogenate complexes.<sup>37</sup>

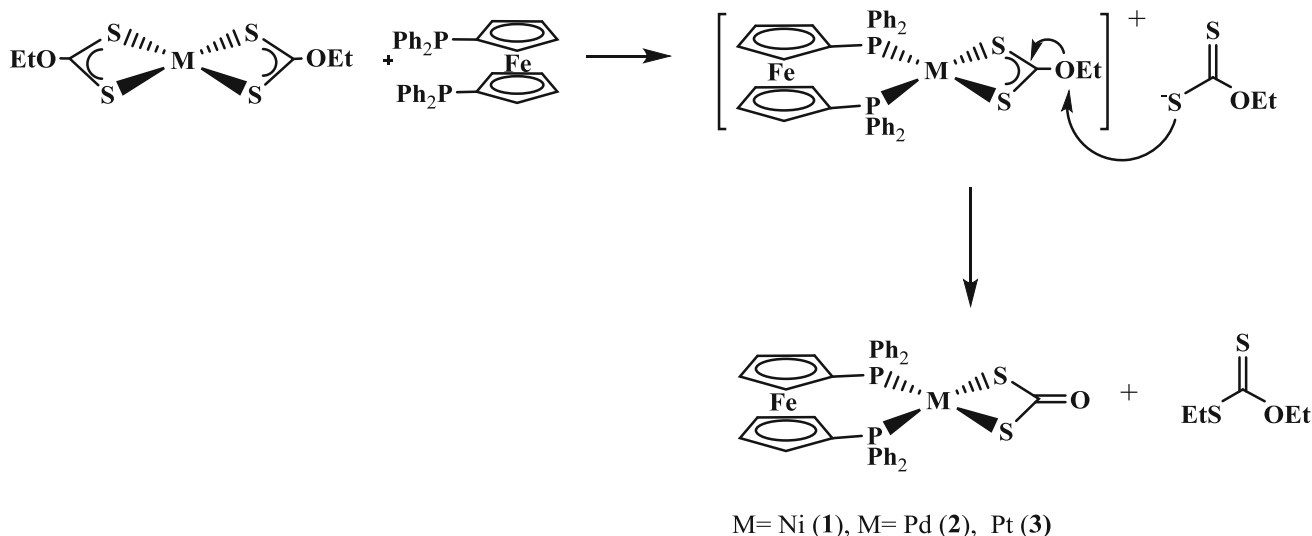
**Table 1.** Crystal data and refinement details for the X-ray structure determinations of **1–3**.

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>35.75</sub> H <sub>29.75</sub> FeNiOP <sub>2</sub> S <sub>2</sub>	C <sub>35</sub> H <sub>28</sub> FeOP <sub>2</sub> PdS <sub>2</sub>	C <sub>35</sub> H <sub>28</sub> FeOP <sub>2</sub> PtS <sub>2</sub>
fw (g•mol <sup>-1</sup> )	715.97	752.88	841.57
T/°C	-140(2)	-140(2)	-140(2)
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	P $\bar{1}$	C 2 2 2 <sub>1</sub>	C 2 2 2 <sub>1</sub>
a/Å	10.9109(2)	11.1196(3)	11.1215(2)
b/Å	15.7089(2)	18.4399(5)	18.4468(3)
c/Å	21.0838(3)	14.6191(3)	14.5793(3)
$\alpha$ /°	108.831(1)	90	90
$\beta$ /°	92.040(1)	90	90
$\gamma$ /°	106.096(1)	90	90
V/Å <sup>3</sup>	3254.98(9)	2997.56(13)	2991.03(10)
Z	4	4	4
$\rho$ (g•cm <sup>-3</sup> )	1.461	1.668	1.869
$\mu$ (cm <sup>-1</sup> )	12.79	13.59	54.33
Measured data	25466	13541	18474
Data with I > 2 $\sigma$ (I)	12619	3269	3218
Unique data (R <sub>int</sub> )	14742/0.0300	3433/0.0332	3432/0.0538
wR <sub>2</sub> (all data, on F <sup>2</sup> ) <sup>a</sup>	0.0947	0.0484	0.0483
R <sub>1</sub> (I > 2 $\sigma$ (I)) <sup>a</sup>	0.0460	0.0255	0.0243
S <sup>b</sup>	1.092	1.044	1.101
Res. dens./e•Å <sup>-3</sup>	1.013/-0.631	0.309/-0.291	0.399/-0.603
Flack-parameter	–	0.44(2)	0.032(6)
Absorpt method	Multi-scan	Multi-scan	Multi-scan
Absorpt corr T <sub>min</sub> /T <sub>max</sub>	0.6901/0.7456	0.7064/0.7456	0.6201/0.7456
CCDC No.	1916199	1916200	1916481

<sup>a</sup>) Definition of the *R* indices:  $R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ;

$wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$  with  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ ;  $P = [2F_c^2 + \text{Max}(F_o^2)]/3$ ;

<sup>b</sup>)  $s = \{ \sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$ .

**Scheme 1.** Synthesis of the {1,1'-bis(diphenylphosphino)ferrocene(dithiocarbamate)} metal complexes **1–3**.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1** presented a singlet at 30.95 ppm for the two equivalent phosphorous atoms which is comparable to that of ( $\kappa^2P,P$ -dppf)NiCl<sub>2</sub> (28.39 ppm). However, the two

phosphorous atoms of **2** and of **3** are not equivalent since the two phosphorous atoms deviate from coplanarity with the Cp-rings. For **2**, two singlets at 29.26 and 35.53 ppm are observed while those of **3**

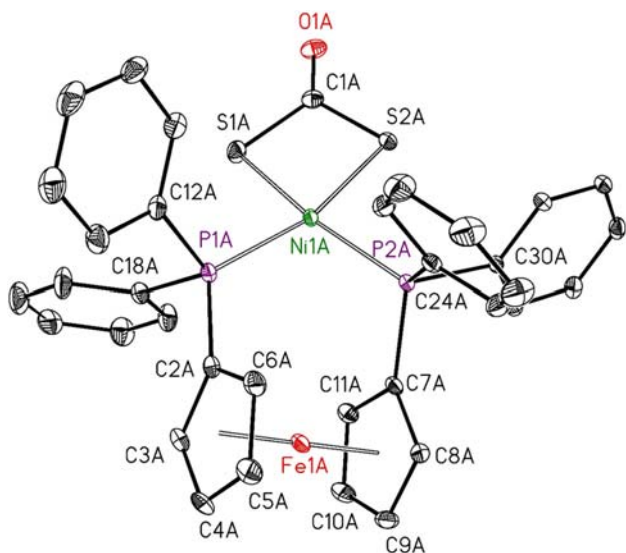
are observed at 12.80 and 15.24 ppm each with a platinum satellite with the platinum-phosphorous coupling of 3767 and 3242 Hz, respectively. These values are comparable to those of  $(\kappa^2P,P\text{-dppf})M(\text{SC}_7\text{H}_4\text{OS})$  ( $M = \text{Pd}$ : 28.5 ppm;  $\text{Pt}$ : 16.5 ppm)<sup>36</sup> and differ from those of  $(\kappa^2P,P\text{-dppf})\text{MCl}_2$  ( $M = \text{Pd}$ : 34.0 ppm;<sup>38</sup>  $\text{Pt}$ : 11.15 ppm).<sup>39</sup>

The IR spectra of complexes **1–3** present a medium peak in the range of 1676 to 1689  $\text{cm}^{-1}$  for the carbonyl group of the dithiocarbonato ligand. This range is similar to those reported for similar systems  $[\text{M}(\kappa^2S,S\text{-S}_2\text{CO})(\text{L})_2]$  ( $\text{L}_2 = (\text{PPh}_3)_2, \text{dppe}$ ).<sup>23,24</sup>

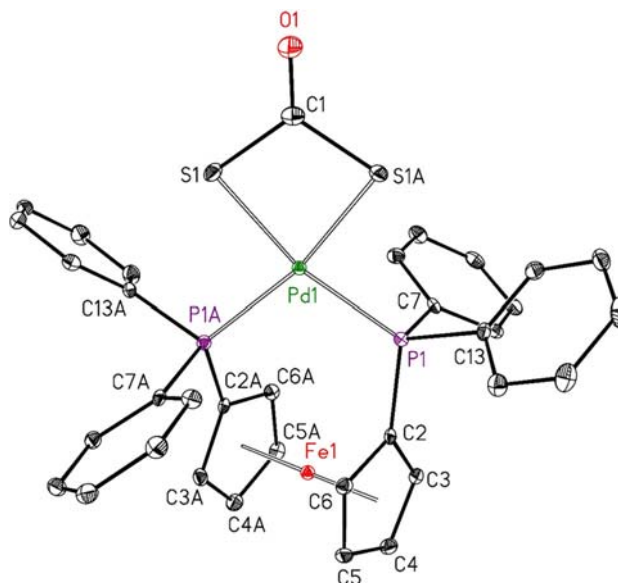
### 3.2 Molecular structure determination

Crystals of each of complexes **1–3** suitable for structure determination are grown by layering hexane over a dichloromethane solution of them. Their structures are shown in Figures 1, 2, 3, respectively. Selected bond lengths and angles of these complexes are presented in Table 2.

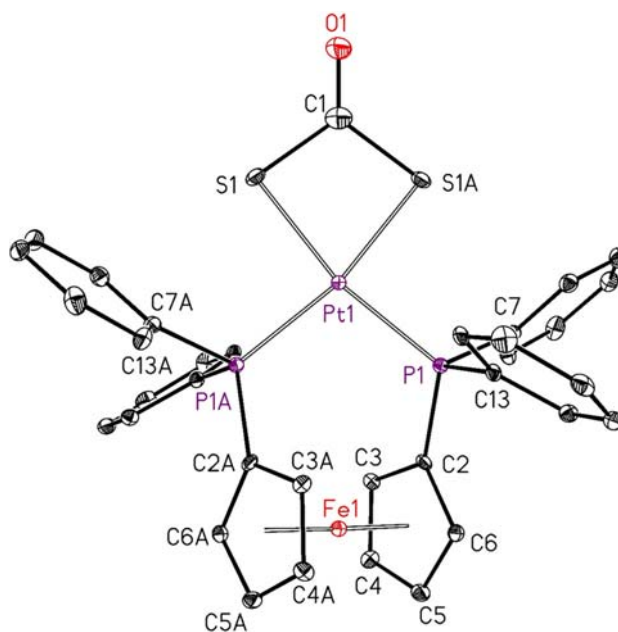
The Ni-S bond lengths of **1** (2.1785(8), 2.2081(9) Å) are shorter than those of the corresponding lengths of  $[\text{Ni}(\kappa^2S,S\text{-S}_2\text{CO})(\kappa^2P,P\text{-}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2))]$  (2.197(1), 2.207(1) Å). Consequently, the Ni-P bond distance of **1** (2.2006(8), 2.2041(8) Å) are longer than that of  $[\text{Ni}(\kappa^2S,S\text{-S}_2\text{CO})(\kappa^2P,P\text{-}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2))]$  (2.165(1), 2.162(2) Å).<sup>40</sup> For **2**, the Pd-S (2.3299(7) Å) and Pd-P (2.3121(7) Å) bond distances are equivalent to the corresponding distances of  $\text{Pd}(\kappa^2S,S\text{-S}_2\text{CO})(\text{PPh}_3)_2$  (Pd-S: 2.340(4), 2.324(3) Å, Pd-P: 2.303(3), 2.337(3) Å).<sup>41</sup> In a similar manner, the Pt-S (2.3369(10) Å) and



**Figure 1.** Molecular structure and atom labelling scheme of **1**. The ellipsoids represent a probability of 30%, H atoms are omitted for clarity reasons.



**Figure 2.** Molecular structure and atom labelling scheme of **2**. The ellipsoids represent a probability of 30%, H atoms are omitted for clarity reasons.



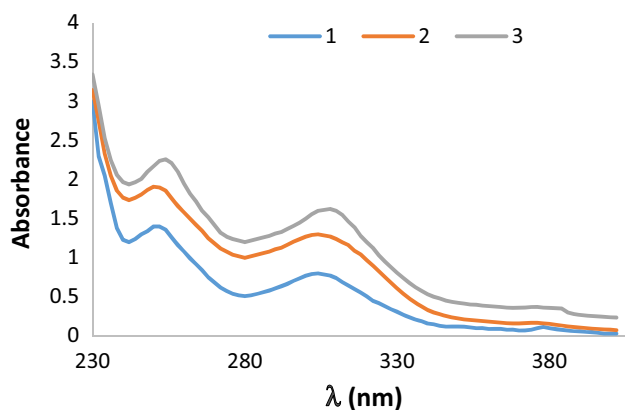
**Figure 3.** Molecular structure and atom labelling scheme of **3**. The ellipsoids represent a probability of 30%, H atoms are omitted for clarity reasons.

Pt-P (2.2825(10) Å) bond distances of **3** are comparable to the corresponding distances of  $\text{Pt}(\kappa^2S,S\text{-S}_2\text{CO})(\text{PPh}_3)_2$  and  $\text{Pt}(\kappa^2S,S\text{-S}_2\text{CO})(\kappa^2P,P\text{-}(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2))$ .<sup>40</sup>

The S-C bond lengths of the three complexes (1.768(3)–1.802(3) Å) are comparable to each other and to those reported for similar systems.<sup>40–42</sup> While the C-O bond of the dithiocarbonato ligand in each of complexes **1–3** is a typical carbon-oxygen double bond and found within the range of those reported for dithiocarbonato complexes.<sup>40–42</sup>

**Table 2.** Selected bond lengths and angles of **1**, **2** and **3**.

Bond distances for <b>1</b>		Bond distances for <b>2</b>		Bond distances for <b>3</b>	
Ni-S	2.1785(8) 2.2081(9)	Pd-S	2.3299(7)	Pt-S	2.3369(10)
Ni-P	2.2006(8) 2.2041(8)	Pd-P	2.3121(7)	Pt-P	2.2825(10)
S-C	1.768(3) 1.767(3)	S-C	1.783(2)	S-C	1.802(3)
O-C	1.203(4)	O-C	1.225(4)	O-C	1.238(6)
Bond angles for <b>1</b>		Bond angles for <b>2</b>		Bond angles for <b>3</b>	
S-Ni-S	79.10(3)	S-Pd-S	76.55(4)	S-Pt-S	76.94(5)
P-Ni-P	102.09(3)	P-Pd-P	101.71(3)	P-Pt-P	101.90(5)
S-Ni-P	90.74(3) 88.82(3)	P-Pd-S	90.95(2)	P-Pt-S	90.63(4)
S-C-S	104.41(17)	S-C-S	108.09(18)	S-C-S	107.6(3)
O-C-S	127.6(3) 128.0(3)	O-C-S	125.95(9)	O-C-S	126.21(14)

**Figure 4.** UV-Vis absorption spectra of  $1.0 \times 10^{-4}$  M **1–3** in  $\text{CH}_2\text{Cl}_2$  using 1 cm path length.

The S-M-S, P-M-P and S-M-P angles indicate a distorted square planar geometry around the metal center. Among these, the smallest angle is the S-M-S angle imposed by the four-membered ring of the ligand, while the P-M-P angle is the largest also imposed by the high steric dppf ligand. The S-C-O and S-C-S bond angles are around  $120^\circ$  indicating a planar dithiocarbonato ligand with  $\text{sp}^2$  hybridized carbon. As expected, the S-C-S angle is compressed as it is part of the four-membered ring leaving the two S-C-O angles to expand.

### 3.3 UV-visible spectroscopy of complexes **1–3**

The electronic absorption spectra of the complexes **1–3** were recorded in dichloromethane solution and are shown in Figure 4. The UV-Vis spectra of the  $\text{MS}_2\text{P}_2$  chromophores showed a strong absorption (252–256 nm) which is assigned to  $\text{M}(\text{II}) \rightarrow \text{L}$  (MLCT)

transition.<sup>24</sup> The other medium absorption band (300–308 nm) can be assigned either to intra-ligand transitions in the  $\text{S}_2\text{CO}$  group<sup>24</sup> or to a metal d-d transition.<sup>38</sup> The very weak band (378–380 nm) may be assigned for a d-d transition of the ferrocene moiety as indicated for similar systems (dppf)PtL (L= 1,3-dithiole-2-thione-4,5-dithiolate, 5,6-dihydro-1,4-dithiin-2,3-dithiolate, 6-hydro-5-phenyl-1,4-dithiin-2,3-dithiolate, 5,6-diphenyl-1,4-dithiin-2,3-dithiolate, 1,2-bis(methylthio)ethylene-1,2-dithiolate, 2,2-dicyano-1,1-ethylenedithiolate).<sup>38,43</sup>

## 4. Conclusions

The dithiocarbonato complexes **1–3** were obtained by C-O bond cleavage of the corresponding *O*-ethyldithiocarbonato metal intermediates. The complexes are fully characterized by spectroscopic techniques (UV-Vis, IR,  $^1\text{H}$ -,  $^{13}\text{C}\{^1\text{H}\}$ -,  $^{31}\text{P}\{^1\text{H}\}$ -NMR) and elemental analysis. The structures of these complexes showed a distorted square planar geometry with the S-M-S bond angle being the smallest and the P-M-P bond angle is the largest.

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