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Synthesis and Analytical Characterization of Novel Pyridyl-Substituted 1,1′-Ethenedithiolato Complexes

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ABSTRACT: *Some 1,1′-ethenedithiolato complexes of nickel(II), palladium(II), and platinum(II) with different phosphine ligands, such as* PPh_3*,* PEt_3*, and dppe were prepared. Starting from 2-, 3- as well as 4-pyridyl methyl ketone, the complexes* **1–15** *were obtained in an one-pot synthesis through reaction with carbon disulfide, using potassium-tert-butylate as a base. They were characterized by* ^1H*,* ^{13}C*, and* ^{31}P *NMR, mass spectra, infrared spectra, and UV–VIS spectra. The molecular structures of the* $(Ph_3P)_2Pd^{II}$ *complex* **9** *containing the 3-pyridyl-ethenedithiolato ligand and of the* $(Et_3P)_2Pt^{II}$ *complex* **12** *containing the 4-pyridyl-ethenedithiolato ligand were determined.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:369–378, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20103

INTRODUCTION

The reactions of carbon disulfide with activated methylene compounds in the presence of bases have been known for many years [1]. The synthesis of 1,1′-ethenedithiolates from substituted acetophenones and carbon disulfide using potassium-*tert*-butylate as a base are described extensively [2–4] and reviewed by Ramadas et al. [5] and by Dieter [6]. The complex chemistry of these 1,1′-ethenedithiolates with Pd(II) and Pt(II) was studied in detail [7].

Different substitution patterns of the aromatic ring offer a wide range of possible reactions. However, 1,1′-ethenedithiolato-complexes, resulting from 2-, 3-, and 4-pyridyl methyl ketone, have not yet been described in the literature to the best of our knowledge. There is only one publication where the 4-pyridyl-β-hydroxydithiocarbonic acid is mentioned [8], but without being characterized. Here we report the synthesis and analytical characterization of novel complexes of Ni^{II}, Pd^{II}, Pt^{II}, containing 2-, 3-, and 4-pyridyl-ethenedithiolato ligands, respectively, with different phosphine ligands (Fig. 1).

RESULTS AND DISCUSSION

Larsson and Lawesson [9] demonstrate a practical way to isolate different β-hydroxy-dithiocarbonic acids. These acids show a fixed enol-structure due to of the strong hydrogen bond between the thioketo moiety and the β-hydroxy hydrogen atom. When deprotonated twice, the enol-structure changes into a keto-structure (Scheme 1), and the resulting 1,1′-ethenedithiolato-ligands can form a metal complex via the sulfur atoms (path A, Scheme 2).

We found that, in our case, a one-pot synthesis of metal complexes was possible without previous isolation of the corresponding dithioacids (path B, Scheme 2).

The potassium-*tert*-butylate was suspended in diethylether and than a mixture of the 2-, 3-, and

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Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

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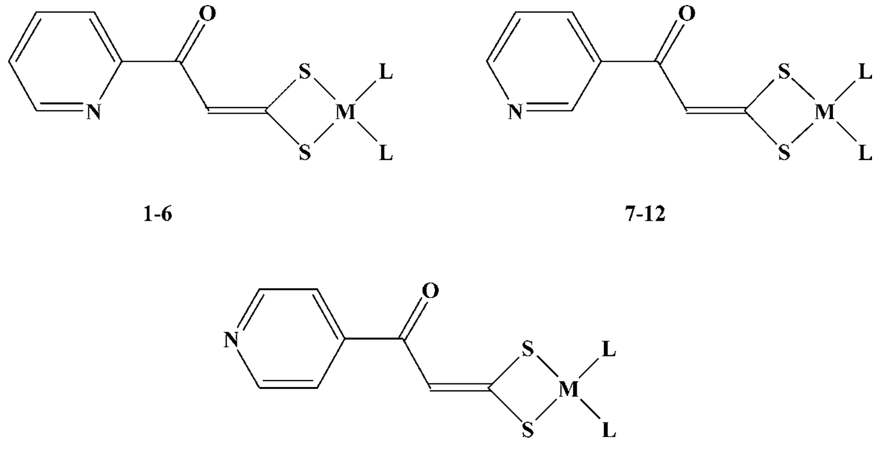


1-6

7-12

13-18

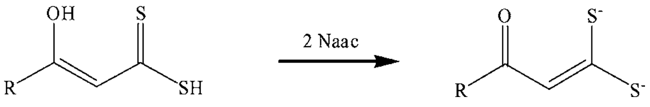
2-Pyridyl-substituted Complexes			3-Pyridyl-substituted Complexes			4-Pyridyl-substituted Complexes		
No.	*M*	*L*	*No.*	*M*	*L*	*No.*	*M*	*L*
1	Pt	PPh_3	**7**	Pt	PPh_3	**13**	Pt	PPh_3
2	Pt	$\frac{1}{2}$ dppe	**8**	Pt	$\frac{1}{2}$ dppe	**14**	Pt	$\frac{1}{2}$ dppe
3	Pt	PEt_3	**9**	Pt	PEt_3	**15**	Pt	PEt_3
4	Pd	PPh_3	**10**	Pd	PPh_3	**16**	Pd	PPh_3
5	Pd	$\frac{1}{2}$ dppe	**11**	Pd	$\frac{1}{2}$ dppe	**17**	Pd	$\frac{1}{2}$ dppe
6	Ni	$\frac{1}{2}$ dppe	**12**	Ni	$\frac{1}{2}$ dppe	**18**	Ni	$\frac{1}{2}$ dppe

FIGURE 1 Synthesized pyridyl substituted 1,1′-ethenedithiolato complexes.

4-pyridyl methyl ketone, respectively, and carbon disulfide was added dropwise at −70°C. After the formation of the intermediate 1,1′-ethenedithiolate, a solution of the corresponding metal salts in dichloromethane was added. The experiments showed that a twofold excess of the corresponding ketone remarkably increased the yield of the complexes. The reaction mixture was stirred for another 2 h at room temperature. The resulting suspension was treated with water, and the organic layer was separated. The side products were separated by washing the organic layer with water until the inorganic layer became colorless. After having dried the organic solution, the solvent was evaporated and the resulting crude product was recryztallized from a mixture of dichloromethane and pentane. All the complexes were obtained as crystalline powders.

With the phosphine ligands, the complexes **1–18** represent a good chemical probe for a characterization by a ^{31}P NMR spectroscopy. In these complexes, the two phosphorus atoms are chemically nonequivalent (Fig. 2).

Thus, the ^{31}P NMR spectra of the platinum complexes show the splitting pattern of an AB spin system with platinum satellites. The typical platinum–phosphorus coupling constants of these complexes are found within a range of 3100 and 3000 Hz (P_A) and 2900 and 2800 Hz (P_B). These values are similar to those found in similar 1,1-ethenedithiolato platinum(II) complexes [10]. Depending on the phosphine ligand used, the phosphorus–phosphorus coupling constants are 11 Hz (dppe), 21 Hz (Et_3P), or 22 Hz (Ph_3P). In the palladium and nickel



SCHEME 1 Change from enol into keto structure.

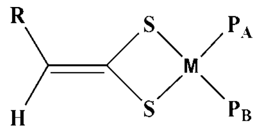
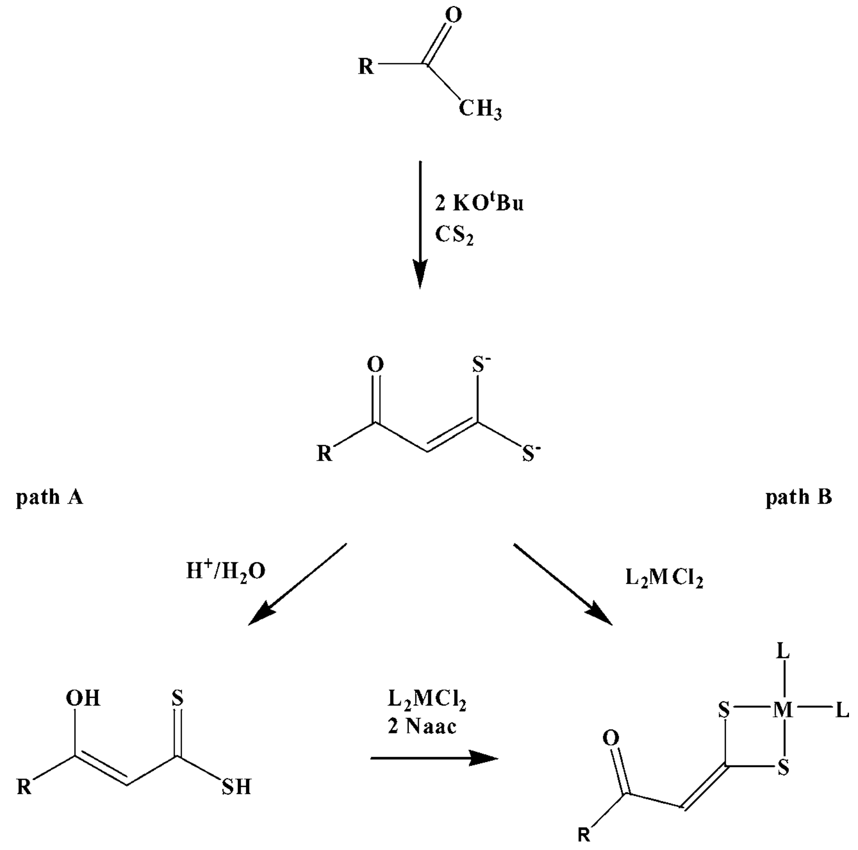


FIGURE 2 Nonequivalent phosphorus atoms.



SCHEME 2 Reaction paths A and B.

complexes, phosphorus–phosphorus coupling constants of 42 Hz (dppePd), 43/44 Hz ($(Ph_3P)_2Pd$), or 32/33 Hz (dppeNi) are observed. The different coupling constants are listed in Table 1.

The ^1H NMR spectra show the typical signals of the pyridyl rings. For the 2- and 3-pyridyl-substituted compounds, a signal can be detected for each proton, whereas the spectra of the 4-pyridyl-substituted complexes present the expected AA′ BB′ spin system.

The important ^1H NMR resonance signals are provided by the methine group. According to the literature studies of free substituted β-hydroxydithiocinnamic acids and their esters [7,9–11], the signals of the complexes should be shifted highfield due to their π-backbonding. This effect can be observed at least in the spectra of the 3- and 4- pyridyl substituted complexes **7–18**, whose signals are detected between $\delta = 6.3$ and 6.6. The ^1H NMR data of the 2-pyridyl substituted complexes **1–6**, on the other hand, offer an interesting aspect. Here, the signals of the methine protons are shifted downfield for nearly 1 ppm.

TABLE 1 ^{31}P NMR Coupling Constants of the Complexes **1–18**

No.	*M*	*L*	*$^1J_{Pt\text{-}P}$ (Hz)*	*$^1J_{Pt\text{-}P}$ (Hz)*	*$^2J_{P\text{-}P}$ (Hz)*
1	Pt	PPh_3	3098	2902	22
2	Pt	PEt_3	2973	2815	21
3	Pt	$\frac{1}{2}$ dppe	2992	2822	11
4	Pd	PPh_3			44
5	Pd	$\frac{1}{2}$ dppe			42
6	Ni	$\frac{1}{2}$ dppe			32
7	Pt	PPh_3	3106	2947	22
8	Pt	PEt_3	2995	2821	21
9	Pt	$\frac{1}{2}$ dppe	3016	2816	10
10	Pd	PPh_3			43
11	Pd	$\frac{1}{2}$ dppe			42
12	Ni	$\frac{1}{2}$ dppe			32
13	Pt	PPh_3	3138	2933	22
14	Pt	PEt_3	2997	2823	21
15	Pt	$\frac{1}{2}$ dppe	3018	2821	11
16	Pd	PPh_3			43
17	Pd	$\frac{1}{2}$ dppe			42
18	Ni	$\frac{1}{2}$ dppe			32

TABLE 2 ^{1}H NMR Signals of the Methine Groups

No.	M	L	δ (=CH—)
1	Pt	PPh_3	7.11
2	Pt	PEt_3	7.23
3	Pt	$\frac{1}{2}$ dppe	7.20
4	Pd	PPh_3	7.11
5	Pd	$\frac{1}{2}$ dppe	7.23
6	Ni	$\frac{1}{2}$ dppe	7.32
7	Pt	PPh_3	6.38
8	Pt	PEt_3	6.48
9	Pt	$\frac{1}{2}$ dppe	6.49
10	Pd	PPh_3	6.60
11	Pd	$\frac{1}{2}$ dppe	6.71
12	Ni	$\frac{1}{2}$ dppe	6.57
13	Pt	PPh_3	6.27
14	Pt	PEt_3	6.47
15	Pt	$\frac{1}{2}$ dppe	6.46
16	Pd	PPh_3	6.58
17	Pd	$\frac{1}{2}$ dppe	6.68
18	Ni	$\frac{1}{2}$ dppe	6.54

A possible explanation could be the interaction between the nitrogen atom in the pyridyl ring and the methine proton. Table 2 illustrates the different NMR shifts of the methine protons.

The ^{13}C NMR data confirm the results of the ^{1}H NMR experiments. Just as the signals of the different pyridyl carbon atoms are observed in their expected range, the signals of the phenyl rings are found in theirs ($\delta = 125$–135). Compared to those in the corresponding acids, the signals of the CS_2 carbon atom are shifted to higher field. In the complexes **1–18**, the ^{13}C NMR spectra exhibit a downfield shifted single resonance of the methine carbon atoms within a range of $\delta = 117$–120 with a $^3J_{\text{C-Pt}}$ coupling (59–75 Hz) and a small $^4J_{\text{C-P}}$ coupling (3.8–5.9 Hz). The C=O signals appear at about $\delta = 186.0$–193.5 and are shifted downfield in contrast to those in the uncoordinated dithioacids [7,9–11]. Table 3 illustrates the different ^{13}C NMR signals and the coupling constants of the methine carbon atom.

The FAB mass spectra of **1–18** show the molecular ions with the expected isotope pattern, the L_2M fragments, as well as the L_2MS fragments.

The IR spectra were recorded in nujol and show the typical absorption bands of the C=O group at about 1580 and 1610 cm^{-1}. This is another evidence for the keto structure of these complexes. Data of these absorption bands are given in Table 4.

The UV–VIS spectra of all the complexes **1–18** show absorption bands in a range of 370–390 nm with values of lg ε at about 4.4. In the palladium (**4, 5, 10, 11, 16, 17**) and nickel (**6, 12, 18**) complexes another absorption band is found at wavelengths around 330 nm (lg ε at about 4.3). Resulting data of the UV–VIS experiments are summarized in Table 5. These results confirm with literature studies [12], and they are typical for intraligand π-π^* transitions.

TABLE 3 Selected ^{13}C NMR Signals and Coupling Constants

No.	M	L	δ (CS_2)	δ (C=O)	δ (=CH—)	$^3J_{C\text{-}Pt}$ (Hz)	$^4J_{C\text{-}P}$ (Hz)
1	Pt	PPh_3	184.4	186.9	118.4	75	5.1
2	Pt	PEt_3	184.2	189.5	119.4	53	4.5
3	Pt	$\frac{1}{2}$ dppe	184.4	185.9	119.4	64	5.0
4	Pd	PPh_3	184.3	190.6	117.9		3.7
5	Pd	$\frac{1}{2}$ dppe	184.3	193.5	119.5		4.3
6	Ni	$\frac{1}{2}$ dppe	185.1	186.7	117.0		4.0
7	Pt	PPh_3	183.7	187.6	119.2	71	5.5
8	Pt	PEt_3	183.4	190.2	119.5	59	5.1
9	Pt	$\frac{1}{2}$ dppe	183.4	191.6	120.0	60	4.9
10	Pd	PPh_3	183.6	191.2	118.0		4.3
11	Pd	$\frac{1}{2}$ dppe	183.4	194.2	119.5		4.2
12	Ni	$\frac{1}{2}$ dppe	184.4	187.5	117.1		3.8
13	Pt	PPh_3	183.5	189.2	118.1	63	5.9
14	Pt	PEt_3	183.3	191.9	119.2	61	4.8
15	Pt	$\frac{1}{2}$ dppe	183.4	193.5	119.8	60	5.5
16	Pd	PPh_3	183.5	192.8	117.8		4.5
17	Pd	$\frac{1}{2}$ dppe	183.3	196.0	119.2		4.3
18	Ni	$\frac{1}{2}$ dppe	184.2	189.2	116.9		4.2

TABLE 4 The IR Absorption Bands of the Carbonyl Group

No.	*M*	*L*	*ν(C=O) (cm^{-1})*	
1	Pt	PPh_3	1616	1579
2	Pt	PEt_3	1619	1580
3	Pt	$\frac{1}{2}$ dppe	1618	1580
4	Pd	PPh_3	1614	1582
5	Pd	$\frac{1}{2}$ dppe	1612	1580
6	Ni	$\frac{1}{2}$ dppe	1617	1578
7	Pt	PPh_3	1619	1583
8	Pt	PEt_3	1609	1579
9	Pt	$\frac{1}{2}$ dppe	1606	1581
10	Pd	PPh_3	1610	1582
11	Pd	$\frac{1}{2}$ dppe	1603	1581
12	Ni	$\frac{1}{2}$ dppe	1607	1579
13	Pt	PPh_3	1609	1586
14	Pt	PEt_3	1609	1587
15	Pt	$\frac{1}{2}$ dppe	1609	1588
16	Pd	PPh_3	1610	1586
17	Pd	$\frac{1}{2}$ dppe	1605	1580
18	Ni	$\frac{1}{2}$ dppe	1612	1593

MOLECULAR STRUCTURES OF THE COMPLEXES **10** *AND* **14**

Slow diffusion of pentane into dichloromethane solutions of the complexes **10** and **14** provided yellow crystals suitable for single-crystal X-ray analysis (Figs. 3 and 4). Regarding the complex **10** (Fig. 3), the following results were received: the C=O bond length with 1.235(7) Å is typical for a carbonyl group. A bond length of 1.366(8) Å represents the C=C double bond between C(1) and C(2), whereas a bond length of 1.423(8) Å is a proof of a single bond between C(2) and C(3). The palladium(II) ion is surrounded by two phosphorus and two sulfur atoms to give a nearly square planar *cis* structure. The data of the bond lengths between Pd and P are 2.301(1) Å and 2.318(1) Å. Regarding Pd and S, the bond lengths are only slightly longer: 2.314(1) Å and 2.336(1) Å. Similar results are received for complex **14**, which are illustrated in Table 6. All these bond lengths are similar to those found in other *cis*-$(Ph_3P)_2M[S_2C{=}CR_2]$ (M = Pd, Pt) complexes [10]. Intermolecular interactions cannot be observed in both the complexes **10** and **14**.

TABLE 5 The Results of the UV–VIS Experiments (CH_2Cl_2)

No.	*M*	*L*	*λ$_{max}$ (nm)*		*lg ε*	
1	Pt	PPh_3	399		4.68	
2	Pt	PEt_3	399		4.30	
3	Pt	$\frac{1}{2}$ dppe	391		4.51	
4	Pd	PPh_3	393	331	4.36	4.30
5	Pd	$\frac{1}{2}$ dppe	386	329	4.49	4.32
6	Ni	$\frac{1}{2}$ dppe	396	343	4.51	4.38
7	Pt	PPh_3	392		4.24	
8	Pt	PEt_3	390		4.35	
9	Pt	$\frac{1}{2}$ dppe	385		4.60	
10	Pd	PPh_3	370	331	4.58	4.51
11	Pd	$\frac{1}{2}$ dppe	378	327	4.55	4.39
12	Ni	$\frac{1}{2}$ dppe	390	340	4.15	4.05
13	Pt	PPh_3	395	340	4.37	4.26
14	Pt	PEt_3	396		4.70	
15	Pt	$\frac{1}{2}$ dppe	391		4.28	
16	Pd	PPh_3	386	330	4.20	4.16
17	Pd	$\frac{1}{2}$ dppe	386	326	3.63	3.45
18	Ni	$\frac{1}{2}$ dppe	396	340	4.55	4.44

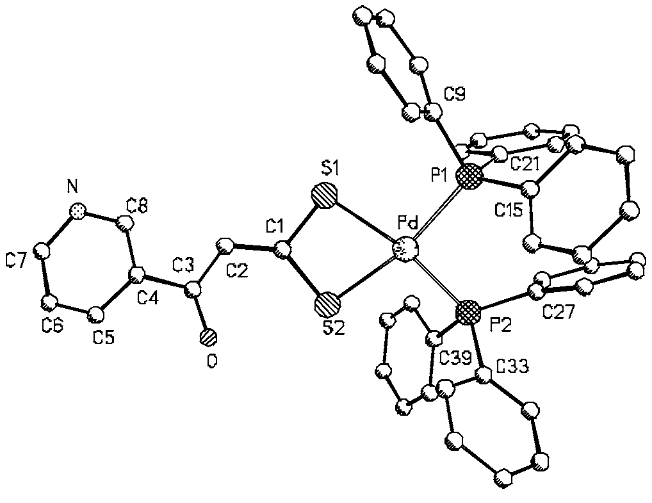


FIGURE 3 The X-ray structure of complex **10**.

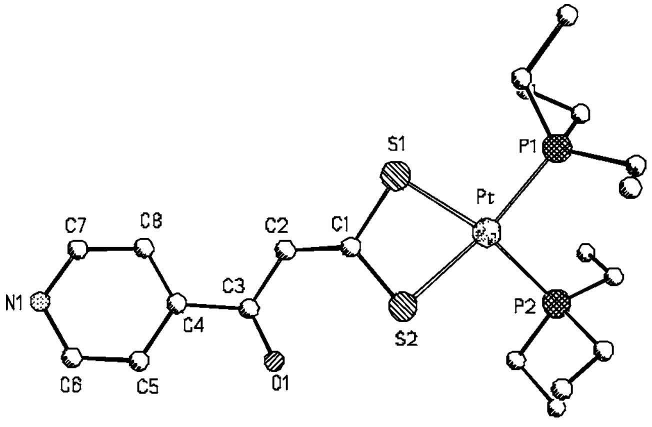


FIGURE 4 The X-ray structure of complex **14**.

TABLE 6 Different Bond Lengths of the Complexes **10–14**

	Bond Lengths (Å)	
	*Complex **10***	*Complex **14***
Bond	Pd PPh$_3$	Pt PEt$_3$
C(3)–O	1.235 (7)	1.228 (6)
C(1)–C (2)	1.366 (8)	1.361 (7)
C(2)–C (3)	1.423 (8)	1.448 (7)
M–P (1)	2.301 (1)	2.281 (1)
M–P (2)	2.318 (1)	2.274 (1)
M–S (1)	2.314 (1)	2.347 (1)
M–S (2)	2.336 (1)	2.348 (1)

CONCLUSION

To summarize, the article is about the preparation of a number of novel pyridyl-substituted 1,1-ethenedithiolato complexes of Ni^{II}, Pd^{II}, Pt^{II} with different phosphine ligands. In the 2-pyridyl-substituted complexes, an interaction between the nitrogen atom and the proton of the methine group is observed. Thus, the nitrogen atoms offer the possibility of further complexation or hydrogen bond interaction in all the complexes **1–18**. So, a first step toward supramolecular chemistry can be done.

EXPERIMENTAL

The resulting complexes **1–18** were synthesized in yields between 35% and 60% referred to the amount of used metal salt. They were isolated as air-stable crystalline substances. All described reactions were conducted under an argon atmosphere, just like the solvents which have been dried conventionally before.

The NMR experiments were carried out with Bruker AVANCE 200 and AVANCE 400 at room temperature. Deuterated chloroform was used as NMR solvent, while the signals of the leftover protons were used as internal standard ($\delta = 7.24$). The mass spectra were recorded at SSQ 10 or MAT95XL, using FAB-ionization. In order to be measured by an IR spectroscopy and to be recorded at Perkin Elmer System 2000 FT-IR spectrometer, the substances were ground in nujol. The UV–VIS experiments were carried out at a Varian CARY 1 UV–Visible spectrophotometer. The elementary analyses are the results of single measurements and were carried out at Heraeus CHNO-Rapid. In the complexes **1, 3–7, 11, 13, 16**, and **18** we could not get better results. The melting points are uncorrected.

The starting products were used without previous purification and the following metal salts were prepared according to the literature procedures: $(Ph_3P)_2PtCl_2$ [13], $(Et_3P)_2PtCl_2$ [14], dppePtCl$_2$ [15], $(Ph_3P)_2PdCl_2$ [16], dppePdCl$_2$, and dppeNiCl$_2$ [17].

General Procedure: A suspension of 224 mg (2 mmol) of potassium-*tert*-butylate in 20 mL of diethylether was cooled down to −70°C. A solution of 121 mg (1 mmol) of the pyridyl methyl ketone and an excess of carbon disulfide 0.08 (1.4 mmol) in 20 mL of diethylether was added dropwise. The color turned to orange. After having stirred for 1 h at −70°C, the mixture was allowed to warm up at room temperature, and then, stirred for another hour, before 0.05 mmol of the metal salt, dissolved or suspended in dichloromethane, was added. The reaction mixture was again stirred for 2 h until 50 mL of water were added. After the separation, the organic layer was washed with water until the inorganic layer became colorless. The organic layer was dried with Na_2SO_4, the solvent evaporated, and the resulting solid was recrystallized from a mixture of dichloromethane and pentane. A crystalline solid was isolated, washed with pentane, and dried in vacuo.

2-Pyridyl-substituted 1,1′-Ethenedithiolato Complexes **1–6**

$C_{44}H_{35}S_2P_2NOPt$ **1** ($M = 914.886$ g/mol), yield: 46% of a green crystalline solid; mp 254°C; Anal. Calcd C: 57.76; H: 3.86; N: 1.53; S: 7.01. Found: C: 56.62; H: 3.86; N: 1.42; S: 6.97%; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.49 (d, $J = 4$ Hz, 1H, H^6), 8.00 (d, $J = 8$ Hz, 1H, H^4), 7.66 (dt, $J_1 = 17$ Hz, $J_2 = 2$ Hz, 1H, H^5), 7.42 (dd, 12H, phenyl-H), 7.29 (q, 1H, H^3), 7.19 (m, 18H, phenyl-H), 7.11 (s, 1H,=CH—); ^{13}C NMR (50 MHz, CDCl$_3$): δ 186.9 (C=O), 184.4 (CS$_2$), 157.0 (C^2), 148.1 (C^6), 136.3 (C^4), 134.5 (m, phenyl-C), 130.7 (d, phenyl-C), 129.4 (dd, phenyl-C), 128.0 (t, phenyl-C), 124.9 (C^5), 122.0 (C^3), 118.4 (=CH—, $^3J_{\text{C-Pt}} = 75$ Hz, $^4J_{\text{C-P}} = 5.1$ Hz); ^{31}P NMR (80 MHz, CDCl$_3$): δ 23.48 ($^1J_{\text{Pt-P}} = 2902$ Hz), 22.18 ($^1J_{\text{Pt-P}} = 3098$ Hz), $^2J_{\text{P-P}} =$ 22 Hz; mass spectra (FAB, nba): $m/z = 916$ ((M + H)$^+$, 2.2%), 751 ((($Ph_3P)_2PtS$)$^+$, 1.6%), 719 ((($Ph_3P)_2Pt$)$^+$, 2.1%); IR (nujol): 1616, 1579 cm^{-1}, s, ν(C=O); UV–VIS (CH$_2$Cl$_2$): $\lambda_{\max}$ (lg ε) = 399 (4.68).

$C_{20}H_{35}S_2P_2NOPt$ **2** ($M = 626.646$ g/mol), yield: 60% of a green crystalline solid; mp 265°C; Anal. Calcd C: 38.33; H: 5.63; N: 2.23; S: 10.23. Found: C: 37.86; H: 5.75; N: 1.84; S: 10.09%; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.58 (d, $J = 5$ Hz, 1H, H^6), 8.12 (d, $J = 7$ Hz, 1H, H^4), 7.73 (dt, $J_1 = 15$ Hz, $J_2 = 2$ Hz, 1H, H^5), 7.28 (q, 1H, H^3), 7.23 (s, 1H, =CH—), 1.85 (m, 12H, —CH$_2$—), 1.15 (m, 18H, —CH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$): δ 189.5 (C=O), 184.2 (CS$_2$), 157.2 (C^2), 148.1 (C^6), 136.3 (C^4), 124.9 (C^5), 122.1 (C^3), 119.4

(=CH—, ${}^3J_{\text{C-Pt}} = 53$ Hz, ${}^4J_{\text{C-P}} = 4.5$ Hz), 16.0 (—CH_2—), 8.1 (—CH_3); ^{31}P NMR (80 MHz, $CDCl_3$): δ 8.93 (${}^1J_{\text{Pt-P}} =$ 2973 Hz), 7.34 (${}^1J_{\text{Pt-P}} = 2815Z$ Hz), ${}^2J_{\text{P-P}} = 21$ Hz; mass spectra (FAB, nba): = 627 ((M + H)$^+$, 58.4%), 463 ((($Et_3P)_2PtS)^+$, 18.7%), 431 ((($Et_3P)_2Pt)^+$, 17.3%); IR (nujol): 1619, 1580 cm^{-1}, s, ν (C=O); UV–VIS (CH_2Cl_2): $\lambda_{\max}$ (lg ε) = 399 (4.30).

$C_{34}H_{29}S_2P_2NOPt$ **3**. ($M = 788.738$ g/mol), yield: 34% of a green crystalline solid; mp 200°C; Anal. Calcd C: 51.77; H: 3.71; N: 1.77; S: 8.13. Found: C: 49.32; H: 3.77; N: 1.71; S: 7.56%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.56 (d, $J = 4$ Hz, 1H, H^6), 8.07 (d, $J = 8$ Hz, 1H, H^4), 7.77–7.68 (m, 10H, H^5, phenyl-H), 7.50–7.36 (m, 14H, H^3, phenyl-H), 7.20 (s, 1H, =CH—), 2.38 (m, 4H, ethylene-H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 185.9 (C=O), 184.4 (CS_2), 157.1 (C^2), 148.1 (C^6), 136.3 (C^4), 132.8 (m, phenyl-C), 131.6 (phenyl-C), 129.1 (d, phenyl-C), 125.0 (C^5), 122.1 (C^3), 119.4 (=CH—, ${}^3J_{\text{C-Pt}} = 64$ Hz, ${}^4J_{\text{C-P}} = 5.0$ Hz), 27.7 (—CH_2—); ^{31}P NMR (80 MHz, $CDCl_3$): δ 44.01 (${}^1J_{\text{Pt-P}} = 2992$ Hz), 42.97 (${}^1J_{\text{Pt-P}} = 2822$ Hz), ${}^2J_{\text{P-P}} = 11$ Hz; mass spectra (FAB, nba): m/z = 789 ((M + H)$^+$, 5.7%), 625 ((dppePtS)$^+$, 2.5%); IR (nujol): 1618, 1580 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): $\lambda_{\max}$ (lg ε) = 391 (4.51).

$C_{44}H_{35}S_2P_2NOPd$ **4** ($M = 826.226$ g/mol), yield: 40% of a green crystalline solid; mp 220°C; Anal. Calcd C: 63.96; H: 4.27; N: 1.69; S: 7.76. Found: C: 61.95; H: 4.34; N: 1.54; S: 7.68%; ^{1}H NMR (200 MHZ, $CDCl_3$): δ 8.49 (d, $J = 4$ Hz, 1H, H^6), 8.02 (d, $J = 5$ Hz, 1H, H^4), 7.65 (dt, $J_1 = 15$ Hz, $J_2 = 2$ Hz, 1H, H^5), 7.45 (dd, 12H, phenyl-H), 7.30 (q, 1H, H^3), 7.19 (m, 18H, phenyl-H), 7.11 (s, 1H, =CH—); ^{13}C NMR (50 MHz, $CDCl_3$): δ 190.6 (C=O), 184.3 (CS_2), 156.7 (C^2), 148.1 (C^6), 136.2 (C^4), 134.4 (m, phenyl-C), 130.6 (d, phenyl-C), 129.8 (dd, phenyl-C), 128.3 (t, phenyl-C), 124.8 (C^5), 121.7 (C^3), 117.9 (=CH—, ${}^4J_{\text{C-P}} = 3.7$ Hz); ^{31}P NMR (160 MHz, $CDCl_3$): δ 33.20, 32.85 (${}^2J_{\text{P-P}} = 44$ Hz); mass spectra (FAB, nba): m/z = 825 (M$^+$, 4.0%), 662 ((($Ph_3P)_2PdS)^+$, 7.7%), 630 ((($Ph_3P)_2Pd)^+$, 5.4%); IR (nujol): 1614, 1582 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): $\lambda_{\max}$ (lg ε) = 393 (4.36), 331 (4.30).

$C_{34}H_{29}S_2P_2NOPd$ **5** ($M = 700.078$ g/mol), yield: 63% of a green crystalline solid; mp 268°C; Anal. Calcd C: 58.33; H: 3.60; N: 2.00; S: 9.16. Found: C: 57.20; H: 4.16; N: 1.96; S: 9.15%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, $J = 4$ Hz, 1H, H^6), 8.10 (d, $J = 8$ Hz, 1H, H^4), 7.76–7.68 (m, 10H, H^5, phenyl-H), 7.43–7.36 (m, 14H, H^3, phenyl-H), 7.23 (s, 1H, =CH—), 2.44 (m, 4H, ethylene-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5 (C=O), 184.3 (CS_2), 156.9 (C^2), 148.1 (C^6), 136.3 (C^4), 132.9 (m, phenyl-C), 131.6 (phenyl-C), 129.3 (m, phenyl-C), 124.9 (C^5), 122.1 (C^3), 119.5 (=CH—, ${}^4J_{\text{C-P}} = 4.3$ Hz), 26.5 (—CH_2—); ^{31}P NMR (80 MHz, $CDCl_3$): δ 53.00, 50.59, ${}^2J_{\text{P-P}} = 42$ Hz; mass spectra (FAB, nba): m/z = 700 ((M + H)$^+$, 11.1%), 536 ((dppePdS)$^+$, 9.7%), 504 ((dppePd)$^+$, 4.7%); IR (nujol): 1612, 1580 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): $\lambda_{\max}$ (lg ε) = 386 (4.49), 329 (4.32).

$C_{34}H_{29}S_2P_2NONi$ **6** ($M = 652.348$ g/mol), yield: 34% of a green crystalline solid; mp 258°C; Anal. Calcd C: 62.59; H: 4.48; N: 2.15; S: 9.83. Found: C: 61.09; H: 4.52; N: 2.19; S: 9.62%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, $J = 4$ Hz, 1H, H^6), 8.03 (d, $J = 8$ Hz, 1H, H^4), 7.78–7.66 (m, 10H, H^5, phenyl-H), 7.42 (m, 14H, H^3, phenyl-H), 7.32 (s, 1H, =CH—), 2.27 (m, 4H, ethylene-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.7 (C=O), 185.1 (CS_2), 156.6 (C^2), 148.1 (C^6), 136.3 (C^4), 133.0 (m, phenyl-C), 131.3 (phenyl-C), 129.1 (d, phenyl-C), 124.9 (C^5), 122.0 (C^3), 117.0 (=CH—, ${}^4J_{\text{C-P}} = 4.0$ Hz), 26.6–25.3 (m, ethylene-C); ^{31}P NMR (160 MHz, $CDCl_3$): δ 59.67, 57.91 (${}^2J_{\text{P-P}} = 32$ Hz); mass spectra (FAB, nba): m/z = 652 ((M + H)$^+$, 18.7%), 488 ((dppeNiS)$^+$, 7.1%); IR (nujol): 1617, 1578 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): $\lambda_{\max}$ (lg ε) = 396 (4.51), 343 (4.38).

3-Pyridyl-substituted 1,1′-Ethenedithiolato Complexes **7–12**

$C_{44}H_{35}S_2P_2NOPt$ **7** ($M = 914.886$ g/mol), yield 30% of a dark yellow crystalline solid; mp 221°C; Anal. Calcd C: 57.76; H: 3.86; N: 1.53; S: 7.01. Found C: 56.21; H: 4.20; N: 1.36; S: 5.44%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (d, $J = 2$ Hz, 1H, H^2), 8.55 (dd, $J_1 = 5$ Hz, $J_2 = 2$ Hz, 1H, H^6), 8.07 (dt, $J_1 = 8$ Hz, $J_2 = 4$ Hz 1H, H^4), 7.67 (dd, $J_1 = 8$ Hz, $J_2 = 6$ Hz, 1H, H^5), 7.63–7.17 (m, 30H, phenyl-H), 6.38 (s, 1H, =CH—); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6 (C=O), 183.7 (CS_2), 151.1 (C^6), 149.1 (C^2), 136.2 (C^3), 135.1 (C^4), 134.5–128.0 (phenyl-C), 123.0 (C^5), 119.2 (=CH—, ${}^3J_{\text{C-Pt}} =$ 71 Hz, ${}^4J_{\text{C-P}} = 5.5$ Hz); ^{31}P NMR (80 MHz, $CDCl_3$): δ 19.44 (${}^1J_{\text{Pt-P}} = 2947$ Hz), 18.27 (${}^1J_{\text{Pt-P}} = 3106$ Hz), ${}^2J_{\text{P-P}} = 22$ Hz; mass spectra (FAB, nba): m/z = 915 ((M + H)$^+$, 5.1%), 718 ((($Ph_3P)_2Pt)^+$, 5.5%); IR (nujol): 1619, 1583 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): $\lambda_{\max}$ (lg ε) = 392 (4.24).

$C_{20}H_{35}S_2P_2NOPt$ **8** ($M = 626.646$ g/mol), yield 43% of a yellow crystalline solid; mp 196°C; Anal. Calcd C: 38.33; H: 5.63; N: 2.23; S: 10.23. Found C: 38.34; H: 5.42; N: 2.22; S: 10.57%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.04 (s, 1H, H^2), 8.58 (d, $J = 4$ Hz, 1H, H^6), 8.14 (d, $J = 8$ Hz, 1H, H^4), 7.26 (dd, $J_1 =$ 12 Hz, $J_2 = 4$ Hz, H^5), 6.48 (s, 1H, =CH—), 1.80 (m, 12H, —CH_2—), 1.14 (m, 18H, —CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 190.2 (C=O), 183.4 (CS_2), 151.1 (C^6), 149.0 (C^2), 136.3 (C^3), 135.1 (C^4), 123.2 (C^5), 119.5 (=CH—, ${}^3J_{\text{C-Pt}} = 59$ Hz, ${}^4J_{\text{C-P}} = 5.1$ Hz), 16.1 (—CH_2—), 8.1 (—CH_3); ^{31}P NMR (80 MHz, $CDCl_3$): δ 9.17 (${}^1J_{\text{Pt-P}} = 2995$ Hz), 7.45 (${}^1J_{\text{Pt-P}} = 2821$ Hz),

$^2J_{\text{P-P}} = 21$ Hz; mass spectra (FAB, nba): *m/z* = 627 ((M + H)$^+$, 100%), 465 ((($Et_3P)_2PtS)^+$, 14.0%), 431 ((($Et_3P)_2Pt)^+$, 31.0%); IR (nujol): 1609, 1579 cm^{-1}, s, ν(C—O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 390 (4.35).

$C_{34}H_{29}S_2P_2NOPt$ **9** (*M* = 788.738 g/mol), yield 40% of a yellow crystalline solid; mp 220°C; Anal. Calcd C: 51.77; H: 3.71; N: 1.77; S: 8.13. Found C: 52.43; H: 3.91; N: 1.60; S: 7.38%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.06 (d, *J* = 1 Hz, 1H, H^2), 8.60 (dd, $J_1 = 5$ Hz, $J_2 = 2$ Hz, 1H, H^6), 8.16 (dt, $J_1 = 6$ Hz, $J_2 = 2$ Hz, 1H, H^4), 7.82–7.28 (m, 21H, phenyl-H, H^5), 6.49 (s, 1H, =CH–, 2.41 (m, 4H,–CH_2–); ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.6 (C=O), 183.4 (CS_2), 151.1 (C^6), 149.0 (C^2), 136.3 (C^3), 135.1 (C^4), 133.2–128.0 (phenyl-C), 123.2 (C^5), 120.0 (=CH–, $^3J_{\text{C-Pt}} = 60$ Hz, $^4J_{\text{C-P}} = 4.9$ Hz), 27.7 (–CH_2–); ^{31}P NMR (80 MHz, $CDCl_3$): δ 44.25 ($^1J_{\text{Pt-P}} = 3016$ Hz), 43.40 ($^1J_{\text{Pt-P}} = 2816$ Hz), $^2J_{\text{P-P}} = 10$ Hz; mass spectra (FAB, nba): *m/z* = 789 ((M + H)$^+$, 11.8%), 625 ((dppePtS)$^+$, 9.6%), 593 ((dppePt)$^+$, 2.6%); IR (nujol): 1606, 1581 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 385 (4.60).

$C_{44}H_{35}S_2P_2NOPd$ **10** (*M* = 826.226 g/mol), yield 58% of a yellow crystalline solid; mp 183°C; Anal. Calcd C: 63.96; H: 4.27; N: 1.69; S: 7.76. Found C: 61.93; H: 4.29; N: 1.69; S: 7.96%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.00 (d, *J* = 1 Hz, 1H, H^2), 8.56 (dd, $J_1 = 5$ Hz, $J_2 = 2$ Hz, 1H, H^6), 8.09 (dt, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H, H^4), 7.43–7.17 (m, 31H, phenyl-H), 6.60 (s, 1H, =CH) ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.2 (C=O), 183.6 (CS_2), 150.9 (C^6), 149.0 (C^2), 135.9 (C^3), 135.0 (C^4), 134.4–128.2 (phenyl-C), 123.0 (C^5), 118.0 (=CH–, $^4J_{\text{C-P}} = 4.3$ Hz); ^{31}P NMR ($CDCl_3$): δ 33.59, 32.63 ($^2J_{\text{P-P}} = 43$ Hz); mass spectra (FAB, nba): *m/z* = 826 ((M + H)$^+$, 3.4%), 662 ((($Ph_3P)_2PdS)^+$, 4.2%), 630 ((($Ph_3P)_2Pd)^+$, 7.6%); IR (nujol): 1610, 1582 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 370 (4.58), 331 (4.51).

$C_{34}H_{29}S_2P_2NOPd$ **11** (*M* = 700.078 g/mol), yield: 48% of a yellow crystalline solid; mp 163°C; Anal. Calcd C: 58.33; H: 3.60; N: 2.00; S: 9.16. Found: C: 57.05; H: 4.11; N: 2.28; S: 10.81%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, *J* = 2 Hz, 1H, H^2), 8.58 (dd, $J_1 = 5$ Hz, $J_2 = 2$ Hz, 1H, H^6), 8.15 (dt, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H, H^4), 7.76–7.25 (m, 21H, phenyl-H, H^5), 6.71 (s, 1H, =CH–, 2.46 (m, 4H,–CH_2–); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2 (C=O), 183.4 (CS_2), 151.0 (C^6), 149.1 (C^2), 136.1 (C^3), 135.0 (C^4), 133.0–129.1 (phenyl-C), 123.1 (C^5), 119.5 (=CH–, $^4J_{\text{C-P}} = 4.2$ Hz), 26.6 (–CH_2–); ^{31}P NMR (160 MHz, $CDCl_3$): δ 53.88, 51.45, $^2J_{\text{P-P}} = 42$ Hz; mass spectra (FAB, nba): *m/z* = 700 ((M + H)$^+$, 6.5%), 536 ((dppePdS)$^+$, 3.0%), 504 ((dppePd)$^+$, 4.7%); IR (nujol): 1603, 1581 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 378 (4.55), 327 (4.39).

$C_{34}H_{29}S_2P_2NONi$ **12** (*M* = 652.348 g/mol), yield 47% of a dark-yellow crystalline solid; mp 224°C; Anal. Calcd C: 62.59; H: 4.48; N: 2.15; S: 9.83. Found C: 63.24; H: 4.66; N: 1.56; S: 8.09%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H, H^2), 8.58 (s, 1H, H^6), 8.10 (s, 1H, H^4), 7.80–7.25 (m, 21H, phenyl-H, H^5), 6.57 (s, 1H, =CH–), 2.29 (m, 4H, –CH_2–); ^{13}C NMR (50 MHz, $CDCl_3$): δ 187.5 (C=O), 184.4 (CS_2), 152.6 (C^6), 149.6 (C^2), 136.7 (C^3), 135.5 (C^4), 133.2–128.0 (phenyl-C), 123.2 (C^5), 117.1 (=CH–, $^4J_{\text{C-P}} = 3.8$ Hz), 25.9 (–CH_2–); ^{31}P NMR ($CDCl_3$): δ 60.16, 58.70 ($^2J_{\text{P-P}} = 33$ Hz); mass spectra (FAB, nba): *m/z* = 652 ((M + H)$^+$, 16.8%); IR (nujol): 1607, 1579 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 390 (4.15), 340 (4.05).

4-Pyridyl-substituted 1,1′-ethenedithiolato complexes **13–18**

$C_{44}H_{35}S_2P_2NOPt$ **13** (*M* = 914.886 g/mol), yield 37% of a yellow crystalline solid; mp 171°C; Anal. Calcd C: 57.76; H: 3.86; N: 1.53; S: 7.01. Found C: 56.87; H: 4.08; N 1.29; S 7.33%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.59 (d, *J* = 5 Hz, 2H, H^2), 7.54 (d, *J* = 6 Hz, 2H, H^3), 7.49–7.20 (m, 30H, phenyl-H), 6.27 (s, 1H, =CH–); ^{13}C NMR (50 MHz, $CDCl_3$): δ 189.2 (C=O), 183.5 (CS_2), 150.3 (C^2), 147.9 (C^4), 134.9–128.4 (phenyl-C), 121.3 (C^3), 118.1 (=CH–, $^3J_{\text{C-Pt}} = 63$ Hz, $^4J_{\text{C-P}} = 5.9$ Hz); ^{31}P NMR (80 MHz, $CDCl_3$): δ 22.60 ($^1J_{\text{Pt-P}} = 2933$ Hz), 21.77 ($^1J_{\text{Pt-P}} = 3138$ Hz), $^2J_{\text{P-P}} = 22$ Hz; mass spectra (FAB, nba): *m/z* = 915 ((M + H)$^+$, 14.0%), 751 ((($Ph_3P)_2PtS)^+$, 6.6%), 719 ((($Ph_3P)_2Pt)^+$, 14.0%); IR (nujol): 1609, 1586 cm^{-1}, s, ν(C=O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 395 (4.37), 340 (4.26).

$C_{20}H_{35}S_2P_2NOPt$ **14** (*M* = 626.646 g/mol), yield 50% of a yellow crystalline solid; mp 149°C; Anal. Calcd C: 38.33; H: 5.63; N: 2.23; S: 10.23. Found C: 37.80; H: 5.47; N: 2.01; S: 9.70%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.63 (d, *J* = 6 Hz, 2H, H^2), 7.66 (d, *J* = 6 Hz, 2H, H^3), 6.47 (s, 1H, =CH–), 1.82 (m, 12H, –CH_2–), 1.18 (m, 18H, –CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 191.9 (C=O), 183.3 (CS_2), 150.1 (C^2), 147.7 (C^4), 121.2 (C^3), 119.2 (=CH–, $^3J_{\text{C-Pt}} = 61$ Hz, $^4J_{\text{C-P}} = 4.8$ Hz), 16.0 (–CH_2–), 8.1 (–CH_3); ^{31}P NMR (80 MHz, $CDCl_3$): δ 9.20 ($^1J_{\text{Pt-P}} = 2997$ Hz), 7.50 ($^1J_{\text{Pt-P}} = 2823$ Hz), $^2J_{\text{P-P}} = 21$ Hz; mass spectra (FAB, nba): *m/z* = 627 ((M + H)$^+$, 71.5%), 463 ((($Et_3P)_2PtS)^+$, 10.8%), 431 ((($Et_3P)_2Pt)^+$, 20.6%); IR (nujol): 1609, 1587 cm^{-1},s, ν(C=O); UV–VIS (CH_2Cl_2): λ_{max} (lg ε) = 396 (4.70).

Crystal Structure Determination

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo K_α radiation. Data were corrected for Lorentz and polarization effects, but only for complex **14** for absorption effects [18, 19].

The structures were solved by direct methods (SHELXS [20]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [21]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [21]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for Complex **10** *[22].* $C_{44}H_{35}NOP_2PdS_2 * CH_2Cl_2$, $M_r = 911.12$ gmol^{-1}, yellow prism, size $0.03 \times 0.03 \times 0.02$ mm^3, triclinic, space group P-1, $a = 10.2091(5)$, $b = 13.0762(7)$, $c = 17.4470(7)$ Å, $\alpha = 101.068(3)$, $\beta = 104.410(2)$, $\gamma = 105.885(3)$ °, $V = 2083.41(17)$ Å^3, $T = -90$°C, $Z = 2$, $\rho_{calcd} = 1.452$ g cm^{-3}, μ (Mo K$_\alpha$) $= 7.86$ cm^{-1}, $F(000) = 928$, 14200 reflections in $h(-12/13)$, $k(-16/16)$, $l(-22/22)$, measured in the range $2.15° \leq \Theta \leq 27.48°$, completeness $\Theta_{max} = 97.1\%$, 9268 independent reflections, $R_{int} = 0.039$, 6362 reflections with $F_o > 4\sigma(F_o)$, 485 parameters, 0 restraints, $R1_{obs} = 0.065$, $wR^2_{obs} = 0.154$, $R1_{all} = 0.106$, $wR^2_{all} = 0.179$, GOOF $= 1.017$, largest difference peak and hole: 2.708/−1.121 e Å^{-3}.

Crystal Data for Complex **14** *[22].* $C_{20}H_{35}NOP_2PtS_2 * CH_2Cl_2$, $M_r = 711.57$ g mol^{-1}, colorless prism, size $0.05 \times 0.04 \times 0.03$ mm^3, orthorhombic, space group $P2_12_12_1$, $a = 11.1869(2)$, $b = 14.6576(3)$, $c = 17.1213(3)$ Å, $V = 2807.43(9)$ Å^3, $T = -90$°C, $Z = 4$, $\rho_{calcd} = 1.684$ g cm^{-3}, μ (Mo K$_\alpha$) $= 54.65$ cm^{-1}, semiempirical, transmin: 0.7411, transmax: 0.8721, $F(000) = 1408$, 6378 reflections in $h(-14/14)$, $k(-18/19)$, $l(-22/22)$, measured in the range $2.58° \leq \Theta \leq 27.49°$, completeness $\Theta_{max} = 99.6\%$, 6378 independent reflections, 5671 reflections with $F_o > 4\sigma(F_o)$, 271 parameters, 0 restraints, $R1_{obs} = 0.034$, $wR^2_{obs} = 0.076$, $R1_{all} = 0.043$, $wR^2_{all} = 0.080$, GOOF $=$ 1.012, Flack-parameter 0.005(8), largest difference peak and hole: 1.268/−1.280 e Å^{-3}.

$C_{34}H_{29}S_2P_2NOPt$ **15** ($M = 788.738$ g/mol), yield 50% of a yellow crystalline solid; mp 175°C; Anal. Calcd C: 51.77; H: 3.71; N: 1.77; S: 8.13. Found C: 51.97; H: 3.69; N: 1.73; S: 8.06%; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.78 (d, $J = 6$ Hz, 2H, H^2), 7.66 (d, $J = 6$ Hz, 2H, H^3), 7.81–7.41 (m, 20H, phenyl-H), 6.46 (s, 1H, =CH—), 2.41 (m, 4H, —CH$_2$—); ^{13}C NMR (50 MHz, CDCl$_3$): δ 193.5 (C=O), 183.4 (CS$_2$), 150.0 (C^2), 147.8 (C^4), 133.1–127.9 (phenyl-C), 121.2 (C^3), 119.8 (=CH—, $^3J_{C\text{-}Pt} = 60$ Hz, $^4J_{C\text{-}P} = 4.9$ Hz), 27.7 (—CH$_2$—); ^{31}P NMR (80 MHz, CDCl$_3$): δ 40.51 ($^1J_{Pt\text{-}P} = 3018$ Hz), 39.66 ($^1J_{Pt\text{-}P} = 2821$ Hz), $^2J_{P\text{-}P} = 11$ Hz; mass spectra (FAB, nba): m/z = 789 ((M + H)$^+$, 3.4%), 625 ((dppePtS)$^+$, 2.2%), 593 ((dppePt)$^+$, 0.8%); IR (nujol): 1609, 1588 cm^{-1}, s, ν(C=O); UV–VIS (CH$_2$Cl$_2$): λ_{max} (lg ε) = 391 (4.28).

$C_{44}H_{35}S_2P_2NOPd$ **16** ($M = 826.226$ g/mol), yield 56% of a yellow crystalline solid; mp 146°C; Anal. Calcd C: 63.96; H: 4.27; N: 1.69; S: 7.76. Found C: 61.18; H: 4.37; N: 1.76; S: 7.75%; ^{1}H NMR (200 MHz, CDCl$_3$): δ 8.59 (d, $J = 6$ Hz, 2H, H^2), 7.60 (d, $J = 6$ Hz, 2H, H^3), 7.43–7.21 (m, 30H, phenyl-H), 6.58 (s, 1H, =CH—); ^{13}C NMR (50 MHz, CDCl$_3$): δ 192.8 (C=O), 183.5 (CS$_2$), 150.0 (C^2), 147.4 (C^4), 134.4–128.2 (phenyl-C), 120.7 (C^3), 117.8 (=CH—, $^4J_{C\text{-}P} = 4.5$ Hz); ^{31}P NMR (CDCl$_3$): δ 33.62, 32.67 ($^2J_{P\text{-}P} = 43$ Hz); mass spectra (FAB, nba): m/z = 826 ((M + H)$^+$, 1.8%), 662 (((Ph$_3$P)$_2$PdS)$^+$, 2.5%), 630 (((Ph$_3$P)$_2$Pd)$^+$, 5.0%); IR (nujol): 1610, 1586 cm^{-1}, s, ν(C=O); UV–VIS (CH$_2$Cl$_2$): λ_{max} (lg ε) = 386 (4.20), 330 (4.16).

$C_{34}H_{29}S_2P_2NOPd$ **17** ($M = 700.078$ g/mol), yield: 72% of a yellow crystalline solid; mp 188°C; Anal. Calcd C: 58.33; H: 3.60; N: 2.00; S: 9.16. Found: C: 58.04; H: 4.16; N: 1.95; S: 9.01%; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.62 (d, $J = 5$ Hz, 1H, H^6), 7.75–7.70 (m, 10H, H^5, phenyl-H), 7.66 (d, $J = 6$ Hz, 1H, H^4), 7.50–7.39 (m, 14H, H^3, phenyl-H), 6.68 (s, 1H, =CH—), 2.48 (m, 4H, ethylene-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 196.0 (C=O), 183.3 (CS$_2$), 150.0 (C^2), 147.5 (C^4), 132.9–129.2 (phenyl-C), 121.2 (C^3), 119.2 (=CH—, $^4J_{C\text{-}P} = 4.3$ Hz); ^{31}P NMR (160 MHz, CDCl$_3$): δ 54.11, 51.74, $^2J_{P\text{-}P} = 42$ Hz; mass spectra (FAB, nba): m/z = 700 ((M + H)$^+$, 5.6%), 536 ((dppePdS)$^+$, 2.8%), 504 ((dppePd)$^+$, 3.6%); IR (nujol): 1605, 1580 cm^{-1}, s, ν(C=O); UV–VIS (CH$_2$Cl$_2$): λ_{max} (lg ε) = 386 (3.63), 326 (3.45).

$C_{34}H_{29}S_2P_2NONi$ **18** ($M = 652.348$ g/mol), yield 57% of a yellow crystalline solid; mp 215°C; Anal. Calcd C: 62.59; H: 4.48; N: 2.15; S: 9.83. Found C: 61.93; H: 4.41; N: 2.18; S: 9.69%; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.60 (s, 2H, H^2), 7.61 (s, 2H, H^3), 7.81–7.40 (m, 20H, phenyl-H), 6.54 (s, 1H, =CH—), 2.29 (m, 4H, —CH$_2$—) ^{13}C NMR (100 MHz, CDCl$_3$): δ 189.2 (C=O), 184.2 (CS$_2$), 150.1 (C^2), 147.1 (C^4), 133.0–129.2 (phenyl-C), 121.2 (C^3), 116.9 (=CH—, $^4J_{C\text{-}P} = 4.2$ Hz), 26.0 (—CH$_2$—); ^{31}P NMR (CDCl$_3$): δ 60.33, 58.82 ($^2J_{P\text{-}P} = 33$ Hz); mass spectra (FAB, nba): m/z = 652 ((M + H)$^+$, 8.2%); IR (nujol): 1612, 1593 cm^{-1}, s, ν(C=O); UV–VIS (CH$_2$Cl$_2$): λ_{max} (lg ε) = 396 (4.55), 340 (4.44).

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[22] CCDC 255329 (complex **10**) and 255328 (complex **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).