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Palladium(II) and Platinum(II) Complexes with Bisphosphanes, $[S_2C{=}C(CN)_2]^{2-}$ and $[Se_2C{=}C(CN)_2]^{2-}$ as Chelating Ligands

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Dedicated to Professor Wolfgang Beck on the Occasion of His 80th Birthday

Keywords: Chelate complexes; 1,1-Dicyanoethylene-2,2-dithiolate; 1,1-Dicyanoethylene-2,2-diselenolate; Palladium; Platinum

Abstract. The palladium(II) and platin(II) 1,1-dicyanoethylene-2,2-dithiolates [(L–L)*M*{$S_2C{=}C(CN)_2$}] (*M* = Pd: L–L = dppm, dppe, dcpe, dpmb; *M* = Pt: dppe, dcpe, dpmb) were prepared either from [(L–L)*M*Cl_2] and $K_2[S_2C{=}C(CN)_2]$ or from [$(PPh_3)_2$*M*{$S_2C{=}C(CN)_2$}] and the bisphosphane. Moreover, [(dppe)Pt{$S_2C{=}C(CN)_2$}] was obtained from [(1,5-C_8H_{12})Pt{$S_2C{=}C(CN)_2$}] and dppe by ligand exchange. The 1,1-dicyanoethylene-2,2-diselenolates [(dppe)*M*{$Se_2C{=}C(CN)_2$}] (*M* = Pd, Pt) were prepared from [(dppe)*M*Cl_2] and $K_2[Se_2C{=}C(CN)_2]$. The oxidation potentials of the square-planar palladium and platinum complexes were determined by cyclic voltammetry. The reaction of [(dcpe)Pd($S_2C{=}O$)] with TCNE led to a ligand fragment exchange and gave the 1,1-dicyanoethylene-2,2-dithiolate [(dcpe)Pd{$S_2C{=}C(CN)_2$}] in good yield.

Introduction

In the context of our work on coordination compounds formed from CS_2 and related heteroallenes,[1] we found that the palladium(0) complex [$(PMe_2Ph)_2$Pd(SCNPh)], formed from [Pd$(PMe_2Ph]_4$ and SCNPh, reacted with a second molecule of SCNPh to afford the palladium(II) derivative [$(PMe_2Ph)_2$Pd(S_2CNPh)] by elimination of CNPh[2]. Analogues of [$(PMe_2Ph)_2$Pd(S_2CNPh)] of the general composition [$(PR_3)_2$*M*(S_2CO)] and [$(PR_3)_2$Pd(S_2CS)] (*M* = Pd, Pt) were well known and had been prepared mainly from [$(PR_3)_2$*M*Cl_2] and alkali salts of the anions $[S_2COMe]^-$ or $[S_2CS]^{2-}$, respectively.[3,4] The nickel complex [(dppe)Ni(S_2CS)] was obtained from [(dppe)Ni(chelate)] precursors and CS_2 as source of the trithiocarbonate ligand.[5]

The aim of the present study was firstly to prepare a series of palladium(II) and platinum(II) compounds [(L–L)Pd($S_2C{=}X$)] and [(L–L)Pt($S_2C{=}X$)], where *X* is $C(CN)_2$ instead of oxygen, sulfur, and NPh, and where L–L is a chelating bisphosphane such as dppe, dcpe etc. Secondly, we were interested to find out whether the counterparts with $[Se_2C{=}C(CN)_2]^{2-}$ as bidentate ligand were also accessible. We point out that whereas some 1,1-dicyanoethylene-2,2-dithiolate platinum(II) complexes [(L–L)Pt{$S_2C{=}C(CN)_2$}] with 1,1′-bis(diphenylphosphanyl)ferrocene,[6] 2,2-bipyridine, 1,10-phenanthroline and their derivatives were described,[7] analogues with 1,1-dicyanoethylene-2,2-diselenolate as ligand, to the best of our knowledge, were unknown.

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Results and Discussion

The bisphosphane metal dichlorides **1a–1d** and **2a–2c** reacted with equimolar amounts of $K_2[S_2C{=}C(CN)_2]$ in THF/CH_2Cl_2 at room temperature to give the four-coordinate chelate complexes **3a–3d** and **4a–4c** in 70–78 % isolated yield (Scheme 1). An alternative procedure used the bis(triphenylphosphane) palladium and platinum dichlorides **5** and **6** as starting materials, which on treating with $K_2[S_2C{=}C(CN)_2]$ afforded the metal 1,1-dicyanoethylene-2,2-dithiolates **7** and **8**. The reactions of **7** with dppe and dpmb, and of **8** with dppe readily led to the displacement of PPh_3 and gave the chelate complexes **3b**, **3d** and **4a**. A similar substitution occurred on treatment of **10** with dppe to furnish **4a** (Scheme 2). In this case, however, the reaction is slower than that of **8** with dppe.

The metal 1,1-dicyanoethylene-2,2-dithiolates **3a–3d, 4a–4c, 7** and **8** are yellow to orange, almost air-stable solids, which are soluble in CH_2Cl_2 and chloroform, but insoluble in hydrocarbons. Characteristic features of the IR spectra of **3a–3d, 4a–4c, 7** and **8** are the strong absorption at 2200–2210 cm^{-1}, corresponding to the C≡N stretching mode, and the band at 1430–1435 cm^{-1}, assigned to an olefinic C=C stretch. Both numbers are in agreement with reference data.[3a] The ^{31}P NMR spectra of **3a–3d, 4a–4c, 7** and **8** display only one signal, confirming the stereochemical equivalence of the phosphane groups. From the satellites in the spectra of the platinum complexes **4a–4c** and **8**, substantially large ^{195}Pt–^{31}P coupling constants of 3000–3170 Hz could be determined. The UV spectra of **3a–3d, 4a–4c, 7** and **8** show a maximum at 340–350 nm, which is at a similar position as found for the palladium and platinum trithionates [(L–L)*M*(S_2CS)] (L–L = dppe, dcpe, dmpe).[8,9]

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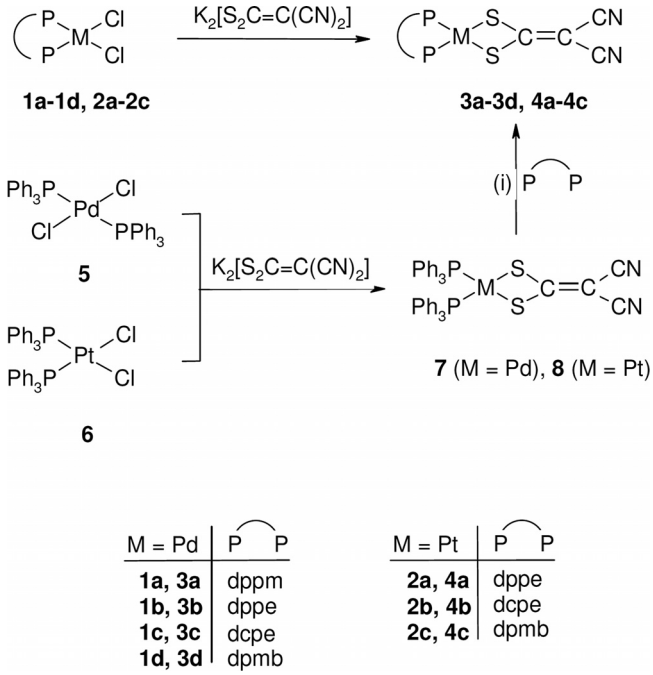
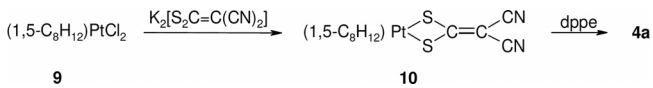
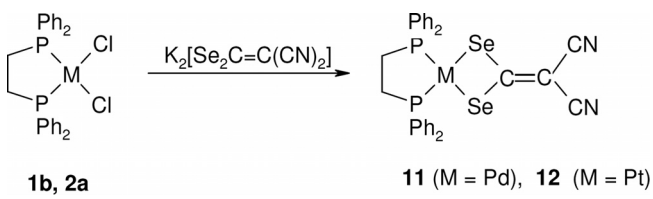


Scheme 1. [(i) *M* = Pd: P–P = dppe. dpmb; *M* = Pt: P–P = dppe].



Scheme 2.

The preparation of the palladium(II) and platinum(II) 1,1-dicyanoethylene-2,2-diselenolates **11** and **12** followed the same route as used for **3b** and **4a** (Scheme 3). Similar to **3a–3d** and **4a–4c**, the diselenolates **11** and **12** are air-stable solids, the IR, UV and ^{31}P NMR spectra of which display only minor differences to those of the analogous metal 1,1-dicyanoethylene-2,2-dithiolates.



Scheme 3.

The X-ray diffraction analyses of **3b** and **11** confirmed that the two related complexes possess the proposed square-planar geometry. The bond angle S–Pd–S in **3b** (74.7(1)°)[10] is considerably smaller than 90° but similar to that in $[(PPh_3)_2Pd\{S_2C=C(CN)_2\}]$ (S–Pd–S = 74.2(2)°),[11] $[(PMe_2Ph)_2Pd(S_2CO)]$ (S–Pd–S = 75.4(1)°),[12] $[(PPh_3)_2Pt(S_2CO)]$ (S–Pt–S = 75.2(2)°),[3a] and analogous coordination compounds with trithiocarbonate as chelating ligand.[13] The bond angle Se–Pd–Se in **11** is only slightly larger than in **3b** and amounts to 77.61(4)°.[14] The Pd–S and Pd–Se distances (**3b**: 2.356(4) and 2.344(4) Å; **11**: 2.425(1) and 2.474(1) Å) are in the range of palladium–sulfur and palladium–selenium single bonds; the Pd–Se distances in **11** being quite similar to those in the maleonitrilediselenoate dianion $[Pd\{Se_2C_2(CN)_2\}_2]^{2-}$.[15] The C=C distances in **3b** (1.370(2) Å) and **11** (1.360(1) Å) are almost similar to those in the structurally analogous platinum(II) complexes $[(1,5\text{-}C_8H_{12})Pt\{S_2C=C(CN)CO_2Et\}]$ (1.368(8) Å),[16] $[(PPh_3)_2Pt\{S_2C=CHC(O)Ph\}]$ (1.349(8) Å)[17] and $[(PC_{16}H_{13})_2Pt\{S_2C=C(CO_2Et)_2\}]$ (1.355(7) Å),[18] and correspond to a carbon–carbon double bond. In the unit cell of **3b**, the molecules are not layered like in $[Pd\{S_2C_2(CN)_2\}_2]^{2-}$ and $[Pt\{S_2C_2(CN)_2\}_2]^{2-}$,[19] which is probably due to the spatial arrangement of the PPh_2 units. The Pd–Pd distances between two neighboring molecules of **3b** are larger than 6.0 Å and thus exclude a direct metal–metal interaction as found in the bis(maleonitrildithiolates).[20]

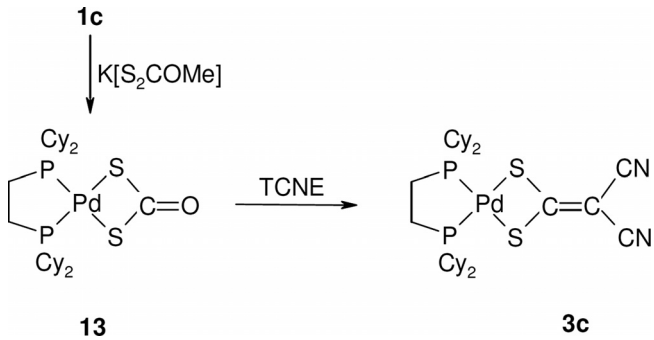
The oxidation chemistry of the palladium and the platinum complexes **3b–3d**, **7**, **11** and **4a–4c**, **8**, **12** were investigated both by electroanalytical and chemical studies. All complexes showed irreversible oxidation waves in acetonitrile at room temperature. As summarized in Table 1, the E_{pa} values for the 1,1-dicyanoethylene-2,2-dithiolates are between 1.51 V and 1.64 V and depend only slightly on the phosphane ligand as well as on the metal atom. The 1,1-dicyanoethylene-2,2-diselenolates **11** and **12** exhibit lower oxidation potentials than their dithiolate counterparts **3b** and **4a**, which can be rationalized by the lower σ-donating capabilities of the dianion $[Se_2C_2(CN)_2]^{2-}$ compared with $[S_2C_2(CN)_2]^{2-}$. We note that the E_{pa} values of the dithiocarbonates $[(dcpe)M(S_2C=O)]$ (*M* = Pd, Pt) are significantly lower than those of the analogues **3c** and **4b**,[9] which is in agreement with the substantial difference in the electronegativity of oxygen and the $C(CN)_2$ fragment.

Table 1. Oxidation Potentials of 1,1-dicyanoethylene-2,2-dithiolates and 1,1-dicyanoethylene-2,2-diselenolates of palladium(II) and platinum(II) (in acetonitrile, referenced to the ferrocen/ferrocenium redox couple).

Compd	E_{pa} /V_{Fc}	compd	E_{pa} /V_{Fc}
3b	+1.55	**4c**	+1.61
3c	+1.58	**7**	+1.60
3d	+1.58	**8**	+1.63
4a	+1.64	**11**	+1.33
4b	+1.51	**12**	+1.42

Attempts to oxidize the compounds **3b** and **4a** by chemical means and trap the proposed paramagnetic cations $[(dppe)M\{S_2C=C(CN)_2\}]^+$ in the presence of $NH_4[PF_6]$ or $Na[BPh_4]$ failed. The reaction of **3b** with equimolar amounts of chloroanil gave **1b** as the main product, whereas on treatment of **3b** with iodine the corresponding diiodide $[(dppe)PdI_2]$ was obtained. The platinum complex **4a** proved to be inert even in the presence of a tenfold excess of I_2. Also no reaction occurred upon treating **3b** or **3c** with tetracyanoethylene (TCNE) as the electron acceptor. In contrast, the dithiocarbonato complex **13** reacted with TCNE in CH_2Cl_2 to give the 1,1-dicyanoethylene-2,2-dithiolate derivative **3c** (see Scheme 4). A similar reaction occurred between $[(dcpe)Pd(S_2CS)]$ and TCNE, although in this case side prod-

ucts were observed. We assume that the formation of **3c** from **13** and TCNE proceeds by a [2+2] cycloaddition process via a four-membered thietane intermediate. Such intermediates have been observed in the reactions of $[(C_5Me_5)Co(PMe_3)(S_2CS)]$ with TCNE,[9] and of thioketones and thioketenes with electron poor olefins.[20]



Scheme 4.

Experimental Section

General: All experiments were carried out under argon using Schlenk techniques. The starting materials **1a–1d**,[21] **2a–2c**,[21,22] **5**,[23] **6**,[24] **9**,[25] $K_2[S_2C{=}C(CN)_2]$,[26] $K_2[Se_2C{=}C(CN)_2]$[27] and $K[S_2COMe]$[28] were prepared as described in the literature. NMR: Bruker WH 90, JOEL FX 90Q. IR: Perkin–Elmer 397. UV: Hitachi 340. X-ray: Enraf Nonius CAD4 diffractometer, MoK_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.55). Melting points were determined by DTA. Abbreviations used: dppm: $CH_2(PPh_2)_2$; dppe: $1,2\text{-}C_2H_4(PPh_2)_2$; dcpe: $1,2\text{-}C_2H_4(PCy_2)_2$; dpmb: $1,2\text{-}C_6H_4(CH_2PPh_2)_2$; s: singlet; d: doublet; m: multiplet; br: broad signal.

Preparation of [(dppm)Pd{$S_2C{=}C(CN)_2$}] (3a): A solution of **1a** (84 mg, 0.15 mmol) in THF/CH_2Cl_2 (1:3, 40 mL) was treated with $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) and stirred for 1 h at room temperature. The solution was filtered, and the filtrate was evaporated in vacuo. An orange solid was obtained, which was washed three times with hexane (5 mL) and dried; yield 66 mg (70%); m.p. 110 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2205 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 346 nm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 30.4 (s) ppm. $C_{29}H_{22}N_2P_2PdS_2$ (631.0): calcd. C 55.20, H 3.51, N 4.44, S 10.16; found C 55.12, H 3.50, N 4.32, S 10.32 %.

Preparation of [(dppe)Pd{$S_2C{=}C(CN)_2$}] (3b): (a) This compound was prepared as described for **3a**, with **1b** (86 mg, 0.15 mmol) and $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) as starting materials; yield 75 mg (78%). – (b) A solution of **7** (216 mg, 0.28 mmol) in CH_2Cl_2 (40 mL) was treated with dppe (112 mg, 0.28 mmol) and stirred for 4 h at room temperature. It was then worked up as described for (a). Bright yellow solid; yield 159 mg (88%); m.p. 170 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2205 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 342 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.48–7.82 (m, 20 H, C_6H_5), 2.59 (d, 4 H, ^2J(P,H) = 20.5 Hz, CH_2) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 54.5 (s) ppm. $C_{30}H_{24}N_2P_2PdS_2$ (645.0): calcd. C 55.86, H 3.75, N 4.34, S 9.94; found C 55.50, H 3.85, N 4.10, S 9.79 %.

Preparation of [(dcpe)Pd{$S_2C{=}C(CN)_2$}] (3c): This compound was prepared as described for **3a**, with **1c** (90 mg, 0.15 mmol) and $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) as starting materials. Pale yellow solid; yield 75 mg (75%); m.p. 266 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2200 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 340 nm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 81.4 (s) ppm. $C_{30}H_{48}N_2P_2PdS_2$ (669.2): calcd. C 53.84, H 7.23, N 4.19, S 9.58; found C 53.57, H 7.11, N 4.20, S 9.50 %.

Preparation of [(dpmb)Pd{$S_2C{=}C(CN)_2$}] (3d): (a) This compound was prepared as described for **3a**, with **1d** (98 mg, 0.15 mmol) and $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) as starting materials; yield 79 mg (73%). – (b) A solution of **7** (216 mg, 0.28 mmol) in CH_2Cl_2 (40 mL) was treated with dppe (132 mg, 0.28 mmol) and stirred for 4 h at room temperature. It was then worked up as described for (a). Yellow solid; yield 179 mg (89%); m.p. 192 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2205 [ν (CN)], 1435 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 343 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.35–7.70 (m, 24 H, C_6H_4 and C_6H_5), 3.80 (m, 4 H, CH_2) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 15.6 (s) ppm. $C_{36}H_{28}N_2P_2PdS_2$ (721.1): calcd. C 59.96, H 3.91, N 3.88, S 8.89; found C 59.66, H 3.85, N 3.93, S 8.95 %.

Preparation of [(dppe)Pt{$S_2C{=}C(CN)_2$}] (4a): (a) This compound was prepared as described for **3a**, with **2a** (100 mg, 0.15 mmol) and $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) as starting materials; yield 86 mg (78%). – (b) A solution of **8** (241 mg, 0.28 mmol) in CH_2Cl_2 (40 mL) was treated with dppe (112 mg, 0.28 mmol) and stirred for 4 h at room temperature. It was then worked up as described for (a); yield 177 mg (86%). – (c) A solution of **10** (102 mg, 0.23 mmol) in CH_2Cl_2 (25 mL) was treated with dppe (92 mg, 0.23 mmol) and stirred for 18 h at room temperature. Afterwards, it was worked up as described for (a); yield 131 mg (88%); light yellow solid; yield 177 mg (86%); m.p. 275 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2205 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 348 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.39–7.89 (m, 20 H, C_6H_5), 2.52 (d, 4 H, ^2J(P,H) = 17.4, $^3J_{(Pt,H)}$ = 48.4 Hz, CH_2) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 41.3 (s, $^2J_{(Pt,P)}$ = 3058 Hz) ppm. $C_{30}H_{24}N_2P_2PtS_2$ (733.7): calcd. C 49.11, H 3.30, N 3.82, S 8.74; found C 49.23, H 3.49, N 3.67, S 8.85 %.

Preparation of [(dcpe)Pt{$S_2C{=}C(CN)_2$}] (4b): This compound was prepared as described for **3a**, with **2b** (103 mg, 0.15 mmol) and $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) as starting materials. Pale yellow solid; yield 86 mg (76%); m.p. 209 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2200 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 348 nm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 64.3 (s, $^2J_{(Pt,P)}$ = 3005 Hz) ppm. $C_{30}H_{48}N_2P_2PtS_2$ (757.9): calcd. C 47.54, H 6.38, N 3.70, S 8.46; found C 47.45, H 6.41, N 3.57, S 8.45 %.

Preparation of [(dpmb)Pt{$S_2C{=}C(CN)_2$}] (4c): This compound was prepared as described for **3a**, with **2c** (111 mg, 0.15 mmol) and $K_2[S_2C{=}C(CN)_2]$ (66 mg, 0.30 mmol) as starting materials; yield 79 mg (73%); pale yellow solid; yield 92 mg (76%); m.p. 214 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2210 [ν (CN)], 1435 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 349 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.38–7.68 (m, 24 H, C_6H_4 and C_6H_5), 3.95 (m, 4 H, CH_2) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 0.6 (s, $^2J_{(Pt,P)}$ = 3083 Hz) ppm. $C_{36}H_{28}N_2P_2PtS_2$ (809.8): calcd. C 53.40, H 3.49, N 3.46, S 7.92; found C 53.21, H 3.55, N 3.47, S 7.80 %.

Preparation of [$(PPh_3)_2$Pd{$S_2C{=}C(CN)_2$}] (7): A solution of **5** (98 mg, 0.28 mmol) in THF/CH_2Cl_2 (1:3, 40 mL) was treated with $K_2[S_2C{=}C(CN)_2]$ (33 mg, 0.15 mmol) and stirred for 2 h at 40 °C. After the reaction mixture was cooled to room temperature, the solution was filtered, and the filtrate was evaporated in vacuo. An deep yellow solid was obtained, which was washed three times with diethyl

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ether (5 mL) and dried; yield 84 mg (78 %); m.p. 200 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2210 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 346 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.20–7.55 (m, C_6H_5) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 30.4 (s) ppm. $C_{40}H_{30}N_2P_2PdS_2$ (771.2): calcd. C 62.29, H 3.92, N 3.63, S 8.32; found C 61.77, H 4.09, N 3.34, S 8.18 %.

Preparation of [$(PPh_3)_2$Pt{$S_2C=C(CN)_2$}] (8): This compound was prepared as described for **7**, with **6** (111 mg, 0.15 mmol) and $K_2[S_2C=C(CN)_2]$ (33 mg, 0.15 mmol) as starting materials. Yellow solid; yield 93 mg (76 %); m.p. >300 °C. **IR** (KBr): $\tilde{\nu}$ = 2210 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 342 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.18–7.57 (m, C_6H_5) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 17.0 (s, $^2J_{(Pt,P)}$ = 3167 Hz) ppm. $C_{40}H_{30}N_2P_2PtS_2$ (859.9): calcd. S 7.46; found S 7.40 %.

Preparation of [(1,5-C_8H_{12})Pt{$S_2C=C(CN)_2$}] (10): A suspension of **9** (123 mg, 0.33 mmol) and $K_2[S_2C=C(CN)_2]$ (87 mg, 0.40 mmol) in CH_2Cl_2 (25 mL) was stirred for 12 h at 40 °C. After the reaction mixture was cooled to room temperature, it was worked up as described for **7**; light yellow solid; yield 124 mg (85 %); m.p. 210 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2215 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 338 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 5.64 (m, 4 H, CH=CH), 2.56 (br. m, 8 H, CH_2) ppm. $C_{12}H_{12}N_2PtS_2$ (443.5): calcd. C 32.50, H 2.73, N 6.32, S 14.46; found C 32.17, H 2.66, N 6.11, S 14.29 %.

Preparation of [(dppe)Pd{$Se_2C=C(CN)_2$}] (11): This compound was prepared as described for **3a**, with **1b** (104 mg, 0.18 mmol) and $K_2[Se_2C=C(CN)_2]$ (112 mg, 0.36 mmol) as starting materials; reaction time 2 h; orange brown solid; yield 94 mg (71 %); m.p. 164 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2200 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 349 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.33–7.62 (m, 20 H, C_6H_5), 2.56 (d, 4 H, ^2J(P,H) = 20.5 Hz, CH_2) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 55.5 (s) ppm. $C_{30}H_{24}N_2P_2PdSe_2$ (738.8): calcd. C 48.77, H 3.27, N 3.79; found C 48.32, H 3.35, N 3.76 %.

Preparation of [(dppe)Pt{$Se_2C=C(CN)_2$}] (12): This compound was prepared as described for **11**, with **2a** (120 mg, 0.18 mmol) and $K_2[S_2C=C(CN)_2]$ (112 mg, 0.36 mmol) as starting materials; orange brown solid; yield 104 mg (70 %); m.p. 124 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 2200 [ν (CN)], 1430 [ν (C=C)] cm^{-1}. UV (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 354 nm. **^{1}H NMR** (90 MHz, CD_2Cl_2): δ = 7.40–7.88 (m, 20 H, C_6H_5), 2.47 (d, 4 H, ^2J(P,H) = 17.6 Hz, CH_2) ppm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 43.4 (s) ppm. $C_{30}H_{24}N_2P_2PtSe_2$ (827.5): calcd. C 43.55, H 2.92, N 3.39; found C 43.26, H 2.94, N 3.57 %.

Preparation of [(dcpe)Pd($S_2C=CO$)] (13): A solution of **1c** (102 mg, 0.17 mmol) in CH_2Cl_2 (30 mL) was treated with K[S_2CCOMe] (28 mg, 0.19 mmol) and stirred for 6 h at 40 °C. After the reaction mixture was cooled to room temperature, it was worked up as described for **7**; pale yellow solid; yield 87 mg (82 %); m.p. 234 °C (decomp.). **IR** (KBr): $\tilde{\nu}$ = 1600 [ν (CO)] cm^{-1}. **UV** (CH_2Cl_2, 10^{-6} mol/L): λ_{max} = 268 nm. **^{31}P NMR** (36.2 MHz, $CDCl_3$): δ = 78.6 (s) ppm. $C_{27}H_{48}OP_2PdS_2$ (621.2): calcd. C 52.21, H 7.79, S 10.32; found C 52.70, H 8.09, S 10.59 %.

Reaction of 13 with Tetracyanoethylene: A solution of **13** (106 mg, 0.17 mmol) in CH_2Cl_2 (20 mL) was treated with TCNE (26 mg, 0.20 mmol) and stirred for 48 h at room temperature. The solvent was evaporated in vacuo, the residue was dissolved in CH_2Cl_2 (5 mL), and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With CH_2Cl_2 a yellow fraction was eluted, which was dried in vacuo. The remaining pale yellow solid was characterized by IR and ^{31}P NMR spectroscopy as **3c**; yield 82 mg (72 %).

Cyclic Voltammetry: In a glovebox [N(nBu)$_4$]PF_6 and the electroactive species were placed into a thoroughly dried CV cell. At a high purity argon line acetonitrile was added through a gastight syringe. Then a platinum disk working electrode, a platinum wire counter electrode, and a $Hg/HgCl_2$ reference electrode were placed into the solution. The cyclic voltammograms were recorded at scan rates between 50 and 200 mV·sec^{-1} using different starting and switching potentials. For the determination of the oxidation potentials, ferrocene ($E_{1/2}$ = +0.40 V vs. SCE) was added as the internal standard.[29] Cyclic voltammograms were recorded using a Potentioscan Wenking POS 73 model of Bank Electronics with an XY recorder as described by *Feldmann* and *Koberstein*.[30]

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References

[1] Reviews: a) H. Werner, *Coord. Chem. Rev.* **1982**, *43*, 165–185; b) H. Werner, *Angew. Chem.* **1990**, *102*, 1109–1121; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1077–1089.
[2] W. Bertleff, H. Werner, *Chem. Ber.* **1982**, *115*, 1012–1018.
[3] a) J. P. Fackler Jr., W. C. Seidel, *Inorg. Chem.* **1969**, *8*, 1631–1639; b) M. C. Cornock, R. O. Gould, C. L. Jones, J. D. Owen, D. F. Steele, T. A. Stephenson, *J. Chem. Soc. Dalton Trans.* **1977**, 496–501.
[4] a) J. M. Burke, J. P. Fackler Jr., *Inorg. Chem.* **1972**, *11*, 2744–2749; b) I. J. B. Lin, H. W. Chen, J. P. Fackler Jr., *Inorg. Chem.* **1978**, *17*, 394–401.
[5] J. Cámpora, E. Carmona, E. Gutiérrez-Puebla, M. L. Poveda, C. Ruiz, *Organometallics* **1988**, *7*, 2577–2579.
[6] D.-Y. Noh, E.-M. Seo, H.-J. Lee, H.-Y. Jang, M.-G. Choi, Y. H. Kim, J. Hong, *Polyhedron* **2001**, *20*, 1939–1945.
[7] J. A. Zuleta, M. Burberry, R. Eisenberg, *Coord. Chem. Rev.* **1990**, *97*, 47–64.
[8] M. Ebner, H. Werner, *Chem. Ber.* **1986**, *119*, 482–487.
[9] L. Scheller, Dissertation Universität Würzburg **1990**.
[10] a) M. Schulz, Dissertation Universität Würzburg **1991**; b) Tables with selected bond lengths and bond angles, the atomic parameters *x*, *y*, *z*, the isotropic temperature factors *U*(eq), and the anisotropic temperature factors U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12} of **3b** are available by the corresponding author (H. W.) on request.
[11] D. Long, H. Zheng, X. Xin, G. Sakane, T. Shibahara, *Polyhedron* **1997**, *16*, 4305–4311.
[12] H. Werner, W. Bertleff, B. Zimmer-Gasser, U. Schubert, *Chem. Ber.* **1982**, *115*, 1004–1011.
[13] R. P. Burns, F. P. McCullough, C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 211–280.
[14] a) O. Nürnberg, Dissertation Universität Würzburg **1993**; b) Tables with selected bond lengths and bond angles, the atomic parameters *x*, *y*, *z*, the isotropic temperature factors *U*(eq), and the anisotropic temperature factors U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12} of **11** are available by the corresponding author (H. W.) on request.
[15] C. C. McLauchlan, S. D. Robowski, J. A. Ibers, *Inorg. Chem.* **2001**, *40*, 1372–1375.
[16] J. M. Bevilacqua, J. A. Zuleta, R. Eisenberg, *Inorg. Chem.* **1993**, *32*, 3689–3693.
[17] W. Weigand, G. Bosl, K. Polborn, *Chem. Ber.* **1990**, *123*, 1339–1342.

[18] F. Yang, P. E. Fanwick, C. P. Kubiak, *Inorg. Chem.* **2002**, *41*, 4805–4809.
[19] M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbauskas, L. Interrante, *J. Am. Chem. Soc.* **1986**, *108*, 1908–1916.
[20] a) U. Schmidt, K. Kabitzke, I. Boie, C. Osterroht, *Chem. Ber.* **1965**, *98*, 3819–3826; b) M. S. Raasch, *J. Org. Chem.* **1970**, *35*, 3470–3483; c) A. Ohno, T. Koizumi, Y. Akasaki, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 319–325.
[21] J. A. Davies, F. R. Hartley, S. G. Murray, *J. Chem. Soc., Dalton Trans.* **1979**, 1705–1708.
[22] A. D. Westland, *J. Chem. Soc.* **1965**, 3060–3067.
[23] B. E. Mann, B. L. Shaw, R. M. Slade, *J. Chem. Soc. A* **1971**, 2976–2980.
[24] a) J. C. Bailar Jr., H. Itatani, *Inorg. Chem.* **1965**, *4*, 1618–1620; b) U. Nagel, *Chem. Ber.* **1982**, *115*, 1998–1999.
[25] J. X. McDermott, J. F. White, G. M. Whitesides, *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.
[26] R. Gompper, W. Töpfl, *Chem. Ber.* **1962**, *95*, 2861–2870.
[27] K. A. Jensen, L. Henriksen, *Acta Chem. Scand.* **1970**, *24*, 3213–3229.
[28] F. Drawert, K.-H. Reuter, F. Born, *Chem. Ber.* **1960**, *93*, 3056–3065.
[29] C. Elschenbroich, *Organometallics* 3rd. ed., Wiley-VCH, Weinheim, **2006**, pp. 718.
[30] M. Feldmann, E. Koberstein, *Nachr. Chem. Tech. Lab.* **1977**, *6*, 517–522.

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