Synthesis and structures of palladium(II) and platinum(II) complexes containing heterocyclic thiolate ligands formed by cycloaddition reactions of coordinated azides[1]

Angela Fleischer, Alexander Roller, Vladimir B. Arion, Bernhard K. Keppler, and Fabian Mohr

Abstract: The phosphine-stabilized azido complexes $[M(N_3)_2(PTA)_2]$ (M = Pd, Pt; PTA = 1,3,5-triaza–7-phosphaadamantane) were prepared in high yields by a ligand exchange reaction from *cis*-$[Pd(N_3)_2(tmeda)]$ and *cis*-$[Pt(N_3)_2(cod)]$, respectively. The Pd and Pt complexes $[M(N_3)_2(PTA)_2]$ undergo cycloaddition reactions with various isothiocyanates to give complexes containing anionic, S-coordinated tetrazole-thiolate ligands of the type *trans*-$[M(SCN_4R)_2(PTA)_2]$ (M = Pd, Pt; R = Et, allyl, Me, Ph). The molecular structures of several of these derivatives were determined by X-ray crystallography.

Key words: palladium, platinum, thiolate, heterocycle, azide, cycloaddition.

Résumé : On a préparé les complexes azido stabilisés par une phosphine $[M(N_3)_2(PTA)_2]$ [M= Pd, Pt; PTA = 1,3,5-triaza-7-phosphaadamantane] avec des rendements élevés en procédant à une réaction d'échange de ligand à partir respectivement du *cis*-$[Pd(N_3)_2(tmeda)]$ et *cis*-$[Pt(N_3)_2(cod)]$. Les complexes du Pd et du Pt $[M(N_3)_2(PTA)_2]$ subissent des réactions de cycloaddition avec divers isothiocyanates pour conduire à la formation de complexes contenant des ligands anioniques tétrazole-thiolate, S-coordinés, du type *trans*-$[M(SCN_4R)_2(PTA)_2]$ (M = Pd, Pt; R = Et, allyle, Me, Ph). Les structures molécules de plusieurs de ces dérivés ont été déterminées par la diffraction des rayons X.

Mots-clés : palladium, platine, thiolate, hétérocycle, azide, cycloaddition.

[Traduit par la Rédaction]

Introduction

Azido complexes of palladium stabilized by phosphine ligands were first reported by Beck et al. in 1965 (1). In a series of papers, the group showed that the coordinated azido groups undergo cycloaddition reactions with nitriles, alkynes, and isothiocyanates to give metal-coordinated tetrazolates (Chart 1) (2–6). Since then, several groups have studied reactions of phosphine-stabilized Pd and, to a much lesser extent, Pt azido complexes with various nitriles and isocyanides. In contrast, cycloaddition reactions with isothiocyanates have only recently been studied in detail (7–9). These results show that the resulting heterocycle is S-coordinated to the metal (Chart 1) rather than N-coordinated, as originally suggested by Beck and co-workers in 1972 (5). A computational study of the reaction mechanism leading to the S-coordinated tetrazole-thiolato complex has also been carried out (10).

We have been exploring the structures and reactivity of precious metal complexes containing the water-soluble phosphine ligand 1,3,5-triaza–7-phosphaadamantane (PTA) (11–14). In this context, water-soluble Pt(II) complexes containing heterocyclic thiolate ligands showed promising in vitro cytotoxicity against various tumour cell lines (15). To generate a library of new water-soluble Pd and Pt complexes with a variety of substituted tetrazole-thiolates from one common precursor, we investigated the cycloaddition of isothiocyanates to PTA-stabilized Pd and Pt azido complexes. Some preliminary results of this study are reported herein.

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This article is dedicated to my mentor and friend Dick Puddephatt in recognition of his outstanding contributions to the chemistry of the precious metals.

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Results and discussion

The PTA stabilized Pd and Pt bis(azido) complexes $[M(N_3)_2(PTA)_2]$ (M = Pd **1**, Pt **2**) are readily prepared in high yields by displacement of the tmeda or cod ligands from *cis*-$[Pd(N_3)_2(tmeda)]$ and *cis*-$[Pt(N_3)_2(cod)]$, respectively. Both complexes are poorly soluble in water and insoluble in chlorinated solvents, acetone, and alcohols, but readily soluble in DMSO. The $^{31}P\{^1H\}$ NMR spectra of

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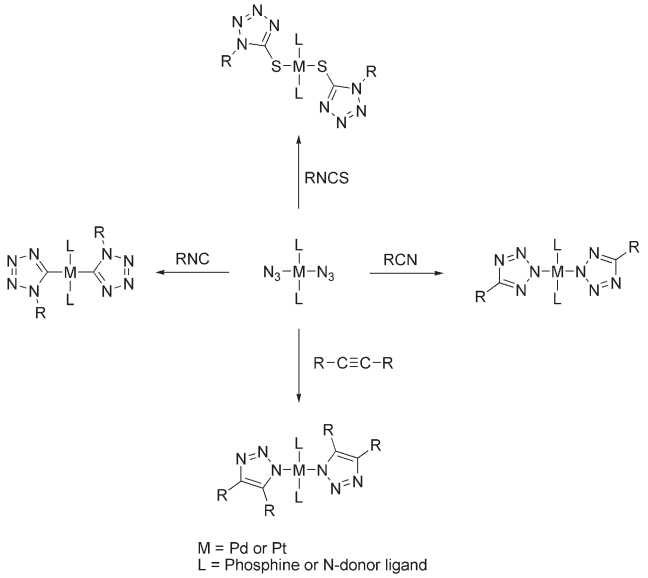
Chart 1.



Scheme 1.

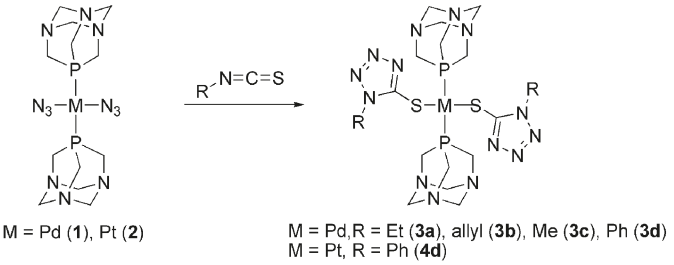
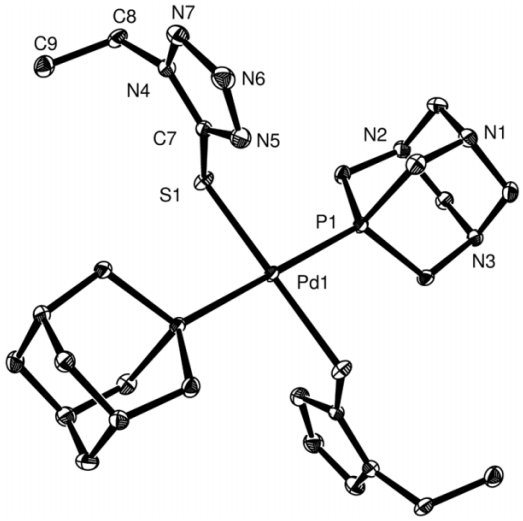


Fig. 1. Molecular structure of complex **3a**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–P1 2.3054(4), Pd1–S1 2.3434(4), S1–C7 1.7250(15), C7–N5 1.3348(18), C7–N4 1.3485(18), N4–N7 1.3576(17), N7–N6 1.2934(18); P1–Pd1–S1 89.390(13), C7–S1–Pd1 100.88(5).



complexes **1** and **2** show singlet resonances at –29.90 and –59.09 ppm, respectively. The IR spectra of both compounds show strong bands between 2020 and 2050 cm^{-1} due to the coordinated azido ligand. The positive ion ES-MS spectra of both complexes show a single, intense peak with *m/z* of 527 (**1**) and 616 (**2**), corresponding to the Na adduct of the molecular ions. The observed isotopic distribution patterns are in perfect agreement with the proposed formulas. Attempts to obtain X-ray diffraction quality crystals of these complexes failed, as the initially yellow or colorless DMSO solutions darkened and eventually decomposed to give a metallic mirror over a period of 2–3 days. However, the solid samples are stable in air at ambient temperatures for months.

Complex **1** reacts with the isothiocyanates RNCS (R = Et, allyl, Me, Ph) in CH_2Cl_2 at room temperature over a period of ca. 18 h to give orange solutions, which, upon layering with Et_2O, afford crystals of the Pd tetrazole-thiolato complexes *trans*-[$Pd(SCN_4R)_2(PTA)_2$] (R = Et **3a**, allyl **3b**, Me **3c**, Ph **3d**) after several days (Scheme 1).

The structures of complexes **3a**, **3b**, and **3d** were determined by X-ray crystallography, and in addition, ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded. Since we were at this stage not interested in isolating bulk samples of the materials, only NMR scale experiments were performed, and thus no other analytical techniques were used to characterize the compounds. In the case of the Me derivative (**3c**), the crystals were of poor quality so only ^1H and $^{31}P\{^1H\}$ NMR spectra are available for this compound. The $^{31}P\{^1H\}$ NMR spectra of complexes **3a**–**3d** consist of a singlet resonance at ca. –56 ppm, which is shifted by ca. 27 ppm from that of the azido precursor. These chemical shifts are very similar to those observed in other Pd PTA complexes containing thiolate ligands (14). The ^1H NMR spectra of complexes **3a**–**3d** show, in addition to the signals from the tetrazole substituents, a singlet and an AB-quartet because of the PCH_2N and NCH_2N protons of the PTA ligands, respectively. The proposed structures of the complexes were confirmed by X-ray diffraction studies of compounds **3a**, **3b**, and **3d**; the molecular structures are shown in Figs. 1–3.

In all three complexes, the palladium is coordinated by two tetrazolate-thiolates (via the sulfur atom) and two PTA ligands in a square planar geometry with a *trans* configuration. The Pd–P and Pd–S bond distances of (ca. 2.30 and 2.34 Å, respectively) are very similar to those observed in other PTA complexes of palladium containing thiolate ligands, e.g., *trans*-[$Pd(SPyridine)_2(PTA)_2$] (14). The C–S bond lengths of ca. 1.72 Å are also similar to those observed in other tetrazole-thiolate complexes of Pd (7) but shorter than in Pd complexes containing pyridine thiolate ligands (1.75 Å) (14).

It was also attempted to prepare analogous complexes using the Pt precursor [$Pt(N_3)_2(PTA)_2$] **2**. In this case, however, the cycloaddition reaction was considerable slower (ca. 2–3 days were required for all of complex **2** to be consumed), compared with the Pd series. This difference in reaction rate between Pd and Pt complexes has also been observed by Kim et al. (7). Furthermore, it was only possible to obtain crystalline material for the product derived from phenyl isothiocyanate (**4d**) upon layering the sample with Et_2O. The spectroscopic data of complex **4d** is essentially identical to that of its Pd congener **3d**. The $^1J_{Pt\text{-}P}$ coupling constant of

Fig. 2. Molecular structure of complex **3b**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–P1 2.2949(4), Pd1–S1 2.3328(4), S1–C7 1.7213(14), C7–N5 1.3472(18), C7–N4 1.3345(18), N4–N7 1.3672(18), N7–N6 1.2944(1); P1–Pd1–S1 93.400(13), C7–S1–Pd1 104.14(5).

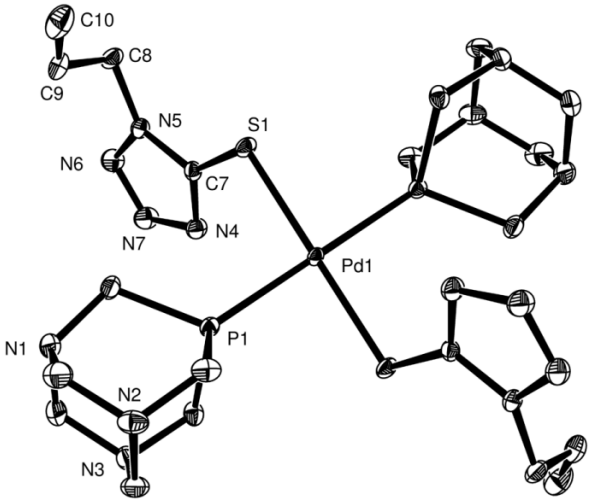
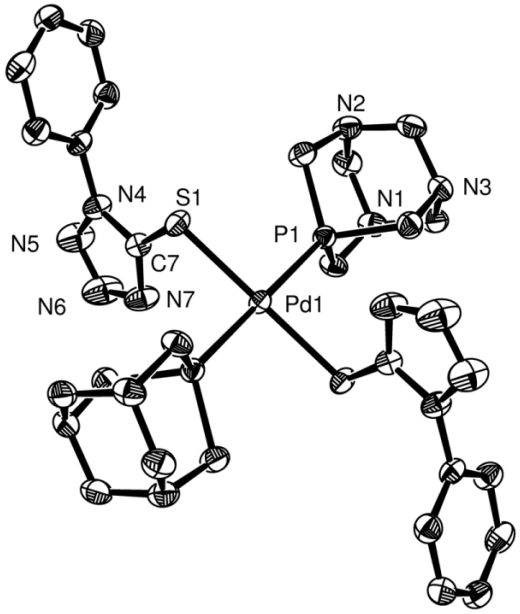
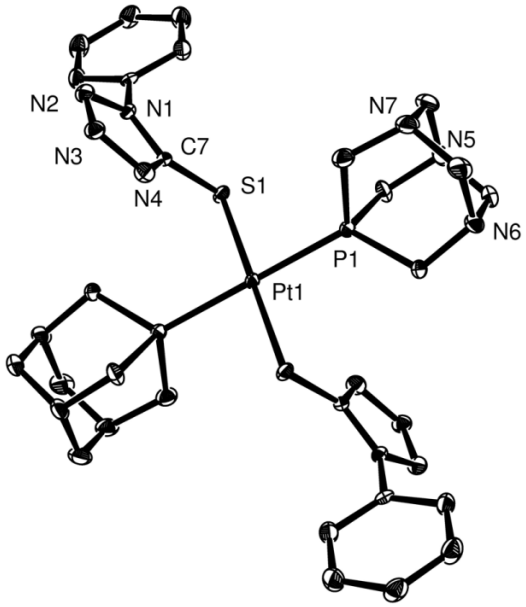


Fig. 3. Molecular structure of complex **3d**. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd1–P1 2.3018(7), Pd1–S1 2.3406(6), S1–C7 1.717(3), C7–N4 1.349(3), C7–N7 1.324(3), N4–N5 1.365(3), N5–N6 1.292(3); P1–Pd1–S1 90.98(2), C7–S1–Pd1 101.29(9).



2458 Hz observed in the $^{31}P\{^{1}H\}$ NMR spectrum of **4d** is consistent with a *trans* configuration, similar to what has been reported for other *trans* Pt complexes containing PTA and thiolate ligands (15). This trans geometry was confirmed by X-ray crystallography; the molecular structure of **4d**·CH_2Cl_2 is shown in Fig. 4.

Fig. 4. Molecular structure of complex **4d**·CH_2Cl_2. Ellipsoids show 50% probability levels. Hydrogen atoms and the disordered CH_2Cl_2 molecule have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt1–P1 2.2897(10), Pt1–S1 2.3393(9), S1-C7 1.717(4), C7–N4 1.331(5), C7–N1 1.355(5), N4–N3 1.364(5), N3–N2 1.282(5); P1–Pt1–S1 87.21(3), C7–S1–Pt1 102.44(13).



The molecular structure of **4d** is very similar to that of the Pd derivative **3d**: Pt shows square planar coordination geometry with a *trans* arrangement of pairs of identical ligands. Bond lengths and angles in **4d** are also typical for complexes of this kind.

In conclusion, we have shown that the reaction of various isothiocyanates with a PTA-stabilized Pd azido complex gives *trans* Pd complexes containing anionic, S-coordinated tetrazole-thiolate ligands. This coordination mode of the cycloaddition product was confirmed by crystallographic studies. In the case of platinum, the same reaction occurs, but the rate of the reaction is considerably slower. Further work is currently in progress to develop a suitable preparation method for larger quantities of these complexes and to study their biological activity.

Experimental

PTA (1,3,5-triaza–7-phosphaadamantane), *cis*-[$Pt(N_3)_2$(cod)] (cod = 1,5-cyclooctadiene), and *cis*-[$Pd(N_3)_2$(tmeda)] (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) were prepared following published procedures (16, 17). All solvents and chemicals were sourced commercially and used as received. ^{1}H, ^{13}C, and $^{31}P\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance III 500 MHz instrument using residual solvent signals as reference. Mass spectra (ES-MS positive ion mode) were measured on a Bruker Esquire 3000 spectrometer and IR spectra on a Bruker FT-IR instrument as KBr disks. Elemental analyses were carried out by staff of the microanalytical laboratory of the Institute of Inorganic Chemistry at the University of Vienna.

[$Pd(N_3)_2(PTA)_2$] (1)

To a CH_2Cl_2 solution of *cis*-[$Pd(N_3)$(tmeda)] (0.300 g, 1.142 mmol) was added a solution of PTA (0.359 g, 2.284 mmol) in CH_2Cl_2 (15 mL). After stirring the mixture for 2 h, the yellow solid was isolated by filtration, washed with Et_2O, and dried. Yield: 0.496 g, 86%. IR (KBr disk, cm^{-1}) ν (N_3): 2040, 2019. ^1H NMR (500 MHz, DMSO-d_6, 25 °C, ppm) δ: 4.47 (AB quart, J = 12.6 Hz, 12 H, NCH_2N), 4.35 (s, 12 H, PCH_2P). $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-d_6, 25 °C, ppm) δ: 51.30 (br s, PCH_2N), 71.64 (s, NCH_2N). $^{31}P\{^1H\}$ NMR (202 MHz, DMSO-d_6, 25 °C, ppm) δ: –29.90. ES-MS *m/z*: 527 $[M + Na]^+$. Calcd. for $C_{12}H_{24}N_{12}P_2Pd$ (504.77): C 28.55, H 4.79, N 33.30; found C 28.72, H 4.81, N 33.06.

[$Pt(N_3)_2(PTA)_2$] (2)

To a suspension of *cis*-[$Pt(N_3)_2$(cod)] (0.100 g, 0.258 mmol) in CH_2Cl_2 was added PTA (0.081 g, 0.516 mmol). After stirring for ca. 2 h, the colourless solid was isolated by filtration, washed with Et_2O, and dried to give 0.129 g (84%) of the complex. IR (KBr disk, cm^{-1}) ν(N_3): 2052, 2036. ^1H NMR (400 MHz, DMSO-d_6, 25 °C, ppm) δ: 4.46 (AB quart, J = 12.6 Hz, 12 H, NCH_2N), 4.25 (s, 12 H, PCH_2P). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6, 25 °C, ppm) δ: –59.09 ($J_{Pt\text{-}P}$ = 3140 Hz). ES MS *m/z*: 616 $[M + Na]^+$. Calcd. for $C_{12}H_{24}N_2P_2Pt$ (593.42): C 24.29, H 4.08, N 28.32; found C 24.50, H 4.03, N 28.39.

Preparation of the cycloaddition products

To a suspension of [$M(N_3)_2(PTA)_2$] (M = Pd, Pt) (25 mg) in CH_2Cl_2 (5 mL) was added an excess (ca. 0.2 mL) of RNCS (R = Et, allyl, Me, Ph). The mixture was left to stir for ca. 18 h at room temperature during which all solid had dissolved. Et_2O was carefully layered onto the solution and after standing for 2–4 days, crystals could be harvested. NMR data was obtained by re-dissolving the crystals in a suitable deuterated solvent. In case of the Pt derivative, the reaction required much longer time (assessed by the time taken for **2** to completely dissolve), and crystals were only obtained when using phenyl isothiocyanate. Using this procedure the following compounds were prepared.

***trans*-[Pd{SCN_4(Et)}$_2$($PTA)_2$] (3a)**

Orange crystals. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 4.34–4.43 (m, 18 H, NCH_2N, CH_3CH_2N), 4.15 (s, 12 H, PCH_2P), 1.58 (t, J = 7.3 Hz, 6 H, CH_3CH_2N). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C, ppm) δ: –56.12.

***trans*-[Pd{$SCN_4(CH_2CHCH_2)$}$_2$($PTA)_2$] (3b)**

Orange crystals. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 5.98–6.09 (m, 2 H, $NCH_2CH{=}CH_2$) 5.39 (d, J = 10.1 Hz, 2 H, $NCH_2CH{=}CH_2$), 5.32 (d, J = 17.0 Hz, 2 H, $NCH_2CH{=}CH_2$), 4.96 (d, J = 5.9 Hz, 4 H, $NCH_2CH{=}CH_2$), 4.38 (AB quart, J = 12.6 Hz, 12 H, NCH_2N), 4.14 (s, 12 H, PCH_2P). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C, ppm) δ: –55.84.

***trans*-[Pd{SCN_4(Me)}$_2$($PTA)_2$] (3c)**

Yellow crystals. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 4.33–4.49 (m, 12 H, NCH_2N), 4.16 (s, 12 H, PCH_2P), 4.00 (s, 6 H, Me). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C, ppm) δ: –56.25.

trans-*[Pd{SCN_4(Ph)}$_2$($PTA)_2$] (3d)*

Orange crystals. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 7.87 (d, J = 7.6 Hz, 4 H, *o*-Ph), 7.60 (t, J = 7.6 Hz, 4 H, *m*-Ph), 7.54 (t, J = 7.3 Hz, 2 H, *p*-Ph), 4.36 (AB quart, J = 13.2 Hz, 12 H, NCH_2N), 4.16 (s, 12 H, PCH_2P). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C, ppm) δ: –55.61.

trans-*[Pt{SCN_4(Ph)}$_2$($PTA)_2$] (4d)*

Colourless crystals. ^1H NMR (500 MHz, $CDCl_3$, 25 °C, ppm) δ: 7.84 (d, J = 7.6 Hz, 4 H, *o*-Ph), 7.62 (t, J = 6.9 Hz, 4 H, *m*-Ph), 7.56 (t, J = 7.3 Hz, 2 H, *p*-Ph), 4.37 (AB quart, J = 13.2 Hz, 12 H, NCH_2N), 4.17 (s, 12 H, PCH_2P). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C, ppm) δ: –63.80 ($J_{P\text{-}Pt}$ = 2458 Hz).

X-ray crystal structure determinations[3]

X-ray diffraction quality crystals of compounds **3a**, **3b**, **3d**, and **4d**·CH_2Cl_2 were mounted in a cryoloop with a drop of oil and placed into the cold stream (100 K) of a Bruker X8 APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), controlled by a Pentium-based PC running the SAINT software package (18). Single crystals were positioned at 40 mm from the detector and 1843, 2075, 1599, and 4656 frames were measured, each for 70, 20, 70, and 5 s over 1° scan width for **3a**, **3b**, **3d**, and **4d**·CH_2Cl_2, correspondingly. Crystal data, data collection parameters, and structure refinement details for **3a**, **3b**, **3d**, and **4d**·CH_2Cl_2 are given in Table 1. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques using the SHELXTL software package (19, 20); scattering factors were taken from the literature (21). The co-crystallized CH_2Cl_2 molecule in **4d**·CH_2Cl_2 was found disordered over two positions with site occupation factors 0.61:0.39. The disorder was solved by using SADI and EADP restraints. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions or localized on difference Fourier maps and isotropically refined. Calculated hydrogen atoms have assigned thermal parameters equal to either 1.5 (methyl hydrogen atoms) or 1.2 (non-methyl hydrogen atoms) times the thermal parameters of the atom to which they were attached. The graphics were prepared by using ORTEP (22).

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[3] Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3806. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml. CCDC 688299–688302 contain the crystallographic data for this manuscript. 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 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic and refinement details of complexes **3a**, **3b**, **3d**, and **4d**·CH_2Cl_2.

Compound	**3a**	**3b**	**3d**	**4d**·CH_2Cl_2
Formula	$C_{18}H_{34}N_{14}P_2PdS_2$	$C_{20}H_{34}N_{14}P_2PdS_2$	$C_{26}H_{34}N_{14}P_2PdS_2$	$C_{28}H_{38}Cl_4N_{14}P_2PtS_2$
FW	679.05	703.07	775.13	1033.67
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$	$P2_1/c$
a (Å)	6.354 10(10)	6.253 40(10)	9.316 2(3)	10.899 8(9)
b (Å)	10.549 5(3)	9.779 7(2)	11.729 2(6)	18.024 0(13)
c (Å)	10.937 8(3)	12.424 9(3)	21.741 0(10)	9.837 1(8)
α (°)	106.484(2)	99.106(2)	90	90
β (°)	92.9180(10)	101.1290(10)	92.048(3)	100.500(5)
γ (°)	106.8810(10)	103.4310(10)	90	90
V (Å^3)	665.62(3)	708.57(3)	1609.63(13)	1900.2(3)
Z	1	1	2	2
D_{calcd} (g cm^{-3})	1.694	1.648	1.599	1.807
μ (mm^{-1})	1.014	0.955	0.850	4.212
F(000)	348	360	792	1024
Reflections	22 043	26 570	48 582	134 597
Unique Reflections (R_{int})	3887 (0.0363)	4154 (0.0385)	4716 (0.0980)	4369 (0.0539)
Parameters	169	178	205	239
θ range (°)	2.40–30.08	2.48–30.05	2.56–30.09	2.21–27.50
R_1 ($I > 2\sigma(I)$)[a]	0.0211	0.0218	0.0394	0.0309
wR_2 (all data)[b]	0.0587	0.0515	0.0920	0.0782
GOF[c]	1.009	1.055	0.984	1.080
Largest diff. peak, hole (e Å^{-3})	0.509, –0.388	0.699, –0.406	0.821, –1.166	1.612, –1.667

[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w (F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

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References

1. W. Beck, K. Feldl, and E. Schuierer. Angew. Chem. Int. Ed. Engl. **4**, 439 (1965).
2. W. Beck, W.P. Fehlhammer, P. Pöllmann, and H. Schächl. Chem. Ber. **102**, 1976 (1969).
3. W. Beck, W.P. Fehlhammer, H. Bock, and M. Bauder. Chem. Ber. **102**, 3637 (1969).
4. W. Beck, K. Burger, and W.P. Fehlhammer. Chem. Ber. **104**, 1816 (1971).
5. P. Kreutzer, J.C. Weis, H. Böhme, T. Kemmerich, W. Beck, C. Spencer, and R.Z. Mason. Naturforsch, **27B**, 745 (1972).
6. P. Kreutzer, J.C. Weis, H. Bock, J. Erbe, and W. Beck. Chem. Ber. **116**, 2691 (1983).
7. Y.J. Kim, J.T. Han, S. Kang, W.S. Han, and S.W. Lee. Dalton Trans. 3357 (2003).
8. Y.J. Kim, X. Chang, J.T. Han, M.S. Lim, and S.W. Lee. Dalton Trans. 3699 (2004).
9. Y.J. Kim, S.H. Lee, S.H. Lee, S.I. Jeon, M.S. Lim, and S.W. Lee. Inorg. Chim. Acta, **358**, 650 (2005).
10. K. Lee, Y.J. Kim, and K.K.J. Baeck. Organomet. Chem. **690**, 4319 (2005).
11. F. Mohr, E. Cerrada, and M. Laguna. Organometallics, **25**, 644 (2006).
12. F. Mohr, S. Sanz, E. Vergara, E. Cerrada, and M. Laguna. Gold Bull. **36**, 212 (2006).
13. F. Mohr, S. Sanz, E.R.T. Tiekink, and M. Laguna. Organometallics, **25**, 3084 (2006).
14. E. Vergara, S. Miranda, F. Mohr, E. Cerrada, E.R.T. Tiekink, P. Romero, and M. Laguna. Eur. J. Inorg. Chem. 2926 (2007).
15. S. Miranda, E. Vergara, F. Mohr, D. de Vos, E. Cerrada, A. Mendía, and M. Laguna. Inorg. Chem. **47**, 5641 (2008).
16. D.J. Daigle. Inorg. Synth. **32**, 40 (1998).
17. Y.J. Kim, J.C. Choi, and K.H. Park. Bull. Korean Chem. Soc. **15**, 690 (1994).
18. Saint-Plus (version 7.06a) and APEX2 [computer programs]. Bruker Nonius AXS Inc., Madison, Wisc., USA. 2004.
19. G.M. Sheldrick. SHELX–97 [computer program]. Program for crystal structure solution. University of Göttingen, Göttingen, Germany. 1997.
20. G.M. Sheldrick. SHELXL–97 [computer program]. Program for crystal structure refinement. University of Göttingen, Göttingen, Germany. 1997.
21. International tables for X-ray crystallography. Vol. *Edited by* C. Kluwer. Academic Press, Dodrecht, The Netherlands. 1992. Tables 4.2.6.8 and 6.1.1.4.
22. G.K. Johnson. Report ORNL–5138. Oak Ridge National Laboratory, Oak Ridge, Tenn., USA. 1976.