Synthesis and Metal Complexes of Thiourea Ligands Containing Carbohydrate-Derived Substituents

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Two glucose-derived thiourea derivatives, **2a** and **2b**, were prepared by addition of the corresponding amino sugars to a solution of 4-nitrobenzoyl isothiocyanate (*Scheme 1*). The thioureas were isolated as colorless solids in good yields and were fully characterized by NMR spectroscopy, optical rotation, elemental analysis, and also by single-crystal X-ray diffraction. Attempts to obtain Cu^{II} and Ni^{II} bis(chelate) complexes with these thioureas failed. However, the C(1)-protected thiourea derivative **2a** reacted with orthopalladated acetato-bridged dimers to afford the corresponding monomeric Pd^{II} complexes **3** and **4** (*Scheme 2*). In these compounds, the thiourea coordinates to the metal as monoanionic O,S chelate ligand, which was confirmed by X-ray crystallography.

Introduction. – Acylthioureas of the type $RC(=O)NHC(=S)NR^2R^3$ are readily deprotonated at the N-atom and may subsequently react with many metal compounds giving metallacyclic compounds in which the thioureas act as monoanionic, O,S chelating ligands or, in the case of gold(I), as monoanionic S^- ligands (*Fig. 1*).

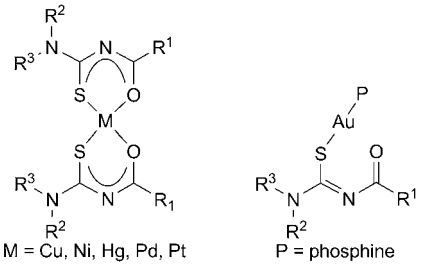


Fig. 1. *General structures of metal complexes containing thioureato ligands*

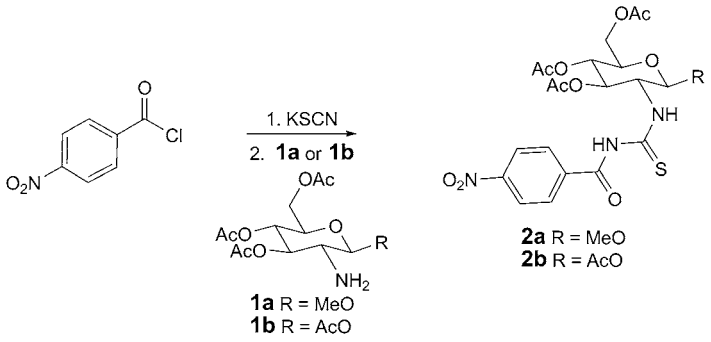
Examples of these types of compounds containing Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II}, Zn^{II}, Co^{III}, Hg^{II} and Rh^{III} have been reported by various groups over the past years [1–15]. In most cases, R^1 corresponds to an aryl group and R^2 and R^3 are alkyl chains or part of a 'cycloalkene' such as morpholine or pyrrolidine. Recent work from our group has shown that these ligands may also act as monoanionic ligands coordinating only through the S-atom to a gold(I) center [16]. The coordination chemistry of thioureas derived from primary amines (*i.e.*, $R^2 = H$) is significantly less developed; only two papers containing structural data for some Pd^{II} and Pt^{II} complexes are available [17][18]. Interest in this class of compounds has arisen from their potential application

as selective extraction agents for metal separation and chromatography [4][10][19][20] and also for their antimicrobial [2][3][21], antimalarial [16][22], and antitumor activity [16][23].

Derivatives of sugars are 'biocompatible' ligands which are of interest in metal complexes for medical applications [24] and also for asymmetric catalysis [25]. The sugar moiety may impart H_2O solubility to the metal complex and/or can be recognized by biological sugar receptors. Examples for sugar functionalized ligands include *Schiff* bases derived from the condensation of amino sugars with pyridine-2-carboxaldehyde or 2-hydroxynaphthalene-1-carboxaldehyde [26][27]. Other groups have studied Mo and Mn complexes containing sugar-substituted pyridine-2-methanols [28] or salen-type ligands (salen = bis(salicyclidene)ethylenediamine) [29] in asymmetric syntheses. A detailed study of the antitumor activity of some Pt^{II} complexes containing glucose derivatives in the backbone has also been reported [30]. Given our interest in the coordination chemistry of thioureas and related sulfur species [1][16][31–36], we wished to prepare some sugar-substituted thioureas and study their reactions with metal compounds. The results of these studies are reported herein.

Results and Discussion. – The glucose-based substituted thiourea derivatives **2a** and **2b** were prepared by addition of the amino sugars **1a** [37] and **1b** [38] to a solution of 4-nitrobenzoyl isothiocyanate generated *in situ* from the corresponding acyl chloride and KSCN in acetone (*Scheme 1*). The thioureas **2a** and **2b** were isolated as colorless solids in good yields and were fully characterized by NMR spectroscopy, optical rotation, elemental analysis, and also by single-crystal X-ray diffraction. The spectroscopic data was fully consistent with the proposed structures. Two distinct signals for the two NH groups were observed in the ^{1}H-NMR spectra of both compounds at δ(H) *ca.* 9 ppm (C(=O)NHC(=S)] and 11 (C(=S)N*H*CH). The signal of the latter was a *d* due to coupling with the H–C(2) of the carbohydrate ring. The H-atom resonances of the carbohydrate ring in both compounds could be unambiguously assigned by using 2D-NMR spectra. Particularly diagnostic was the magnitude of the coupling constant of the signal of H–C(2), since this indicated the configuration of the carbohydrate ring at this position.

Scheme 1



The molecular structures of both compounds **2a** and **2b** were confirmed by X-ray diffraction (*Fig. 2*, *a* and *2*, *b*; *Table*). In both cases, the thiourea unit is attached to the pyranose ring in the equatorial position at C(2) under retention of the glucose configuration. The carbohydrate ring is rotated by *ca.* 90° relative to the thiourea unit, whilst the aromatic ring lies almost in the plane of the thiourea moiety. Both structures are very similar in terms of bond lengths and angles as well as in the orientation of the C=O and C=S units with respect to each other. In both compounds, the HNC(=S)NHC(=O) unit lies in one plane and is rotated such that the chalcogen atoms lie on opposite sides (*Fig. 3*). This conformation is (in both molecules) held in place by an intramolecular H-bond between N(1) and O(1) with H···O distances of *ca.* 1.97 and 1.82 Å, respectively. A similar structural arrangement including such an intramolecular H-bond has also been found in the cyclohexyl (Cy) derivative 4-$O_2NC_6H_4C(=O)NHC(=S)NHCy$ [39]. In addition to this intramolecular H-bond, a further intermolecular H-bond between N(2)–H and the pyranose ring O-atom in **2a** (H···O 2.48 Å) or the solvated-ethanol O-atom in **2b** (H···O 2.43 Å) is observed. The OH group of the ethanol solvent molecule is involved in a further O–H···O H-bond to the carbonyl O-atom of the C(6) *O*-acetyl protecting group.

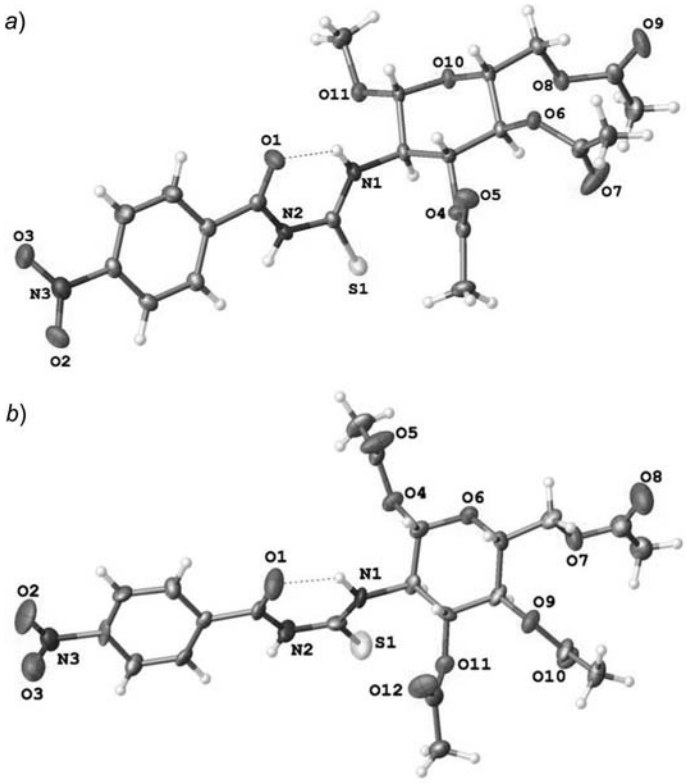


Fig. 2. *Molecular structure of* a) **2a** *and* b) **2b**. Arbitrary atom numbering; 50% probability ellipsoids; the EtOH of solvation for **2b** is omitted for clarity.

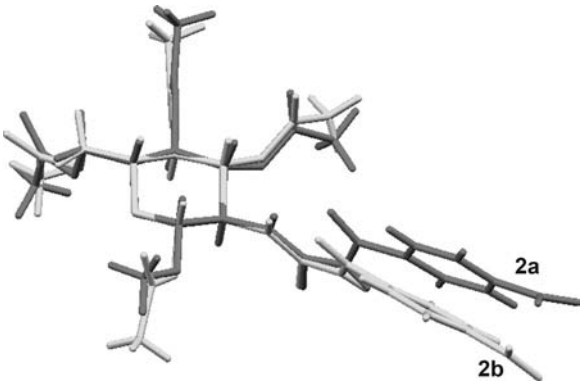


Fig. 3. *Superposition of the molecular structures of* **2a** *and* **2b**. The r.m.s. of the fitted pyranose ring atoms is 0.067 Å.

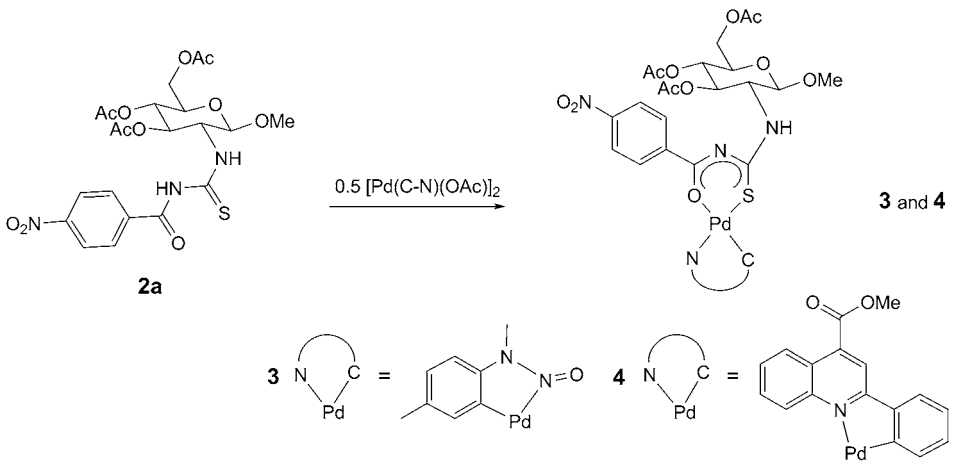
Table. *Crystal Data and Structure Refinement for Compounds* **2a**, **2b**, *and* **4**

	2a	**2b**	**4**
Empirical formula	$C_{21}H_{25}N_3O_{11}S$	$C_{24}H_{31}N_3O_{13}S$	$C_{38}H_{36}N_4O_{13}PdS$
M_r	527.50	601.58	895.17
Crystal system	tetragonal	monoclinic	monoclinic
Space group	$P4_32_12$	$P2_1$	$P2_1$
a [Å]	11.3362(3)	11.003(4)	5.3581(11)
b [Å]	11.3362(3)	10.502(4)	28.747(6)
c [Å]	37.866(3)	12.739(5)	12.166(3)
β [°]		103.97(3)	93.311(3)
V [Å^3]	4866.1(4)	1428.5(9)	1870.8(7)
Z	8	2	2
Density (calc.) [Mg/m^3]	1.440	1.399	1.589
Absorption coefficient [mm^{-1}]	0.198	0.183	0.626
$F(000)$	2208.0	632.0	916.0
Crystal size [mm]	$0.21 \times 0.18 \times 0.04$	$0.06 \times 0.05 \times 0.01$	$0.036 \times 0.028 \times 0.001$
2Θ range [°]	6.48 – 58.82	5.86 – 58.82	1.82 – 31.17
Reflections collected	11365	6456	50201
Independent reflections	5611	4916	11998
R(int)	0.0412	0.0718	0.0707
Data, restraints, parameters	5611, 0, 329	4916, 1, 380	11998, 1, 519
Goodness-of-fit on F^2	1.076	0.720	1.160
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0568$, $wR_2 = 0.1078$	$R_1 = 0.0590$, $wR_2 = 0.1081$	$R_1 = 0.0520$, $wR_2 = 0.1352$
R indices (all data)	$R_1 = 0.0760$, $wR_2 = 0.1128$	$R_1 = 0.1768$, $wR_2 = 0.1300$	$R_1 = 0.0725$, $wR_2 = 0.1662$
Absolute structure parameter (*Flack*) [40]	0.05(12)	0.01(18)	0.03(3)
Largest diff. peak and hole [e Å^{-3}]	0.23 and – 0.30	0.37 and – 0.32	2.18 and – 2.53

We initially attempted the reaction of **2a** and **2b** with $[Cu(OAc)_2]$ in the hope to obtain homoleptic bis(chelate) complexes containing the deprotonated thioureas. However, in both cases examination of the reaction mixture by electrospray mass

spectrometry showed a multitude of signals, the majority of which could not be assigned. We were able to identify signals corresponding to Cu^{II} adducts of the thioureas accompanied by loss of one or more acetate groups or loss of the entire carbohydrate unit. Similar results were also obtained with $[Ni(OAc)_2]$. It seemed, therefore, that under these conditions, the ligands undergo fragmentation and also lose the acetate groups. From these preliminary experiments, it also became clear that the tetraacetate derivative **2b** had a much greater tendency to undergo fragmentation than **2a**, we therefore focused our attention on the reactivity of **2a** with acetato-bridged cyclopalladated compounds. Similar reactions of thiourea derivatives with cyclopalladated acetato-bridged dimers have been previously reported by us [32]. Thus, the reaction of **2a** with 1/2 equiv. of the cyclopalladated dimers gave the yellow Pd^{II} complexes **3** and **4** in good yields (*Scheme 2*). The compounds were characterized by ^{1}H-NMR spectroscopy, elemental analysis and, in the case of **4** by X-ray crystallography. The ^{1}H-NMR spectra of **3** and **4** revealed that the signal of the NH H-atom between the CO and CS groups had disappeared, consistent with deprotonation of the thiourea unit. The second NH signal was still visible as a *d* due to coupling with the carbohydrate ring H–C(2). The coupling constant for this NH H-atom (*ca.* 9.3 Hz) was equal in both the Pd-complexes as well as in the unchelated thioureas, indicating that the configuration at C(2) of the sugar moiety died not change during the reaction. This was further confirmed by an X-ray diffraction study of **4** (*Table*). The molecule crystallizes in space group $P2_1$ and consists of a Pd-atom coordinated to the *ortho*-C-atom of the phenyl substituent at the quinoline derivative, the N-atom of the quinoline unit, as well as the S- and O-atoms of the deprotonated thiourea ligand (*Fig. 4*). Overall, the coordination geometry about the Pd center is, as expected, square planar. The thiourea ligand is deprotonated at N(1) and forms a planar O,S-chelate ring, typical for this type of ligand. The bond lengths and angles about the Pd-atom in **4** are similar to those observed previously in other cyclopalladated thioureato complexes [32].

Scheme 2



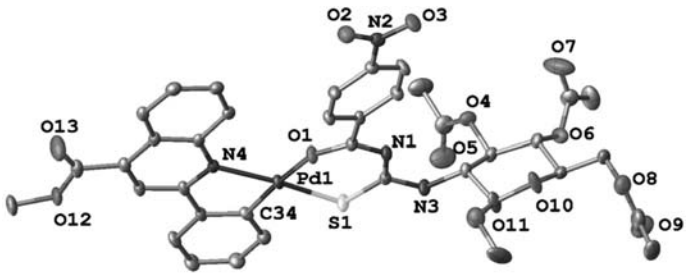


Fig. 4. *Molecular structure of* **4**. Arbitrary atom numbering; 50% probability ellipsoids; H-atoms are omitted for clarity.

Conclusions. – We prepared and fully characterized two carbohydrate-substituted thioureas and examined their reactivity with metal species. Reactions with metal acetates led to fragmentation of the ligands and not to the expected bis(chelate) metal complexes. However, the reaction with cyclometallated palladium(II) complexes cleanly afforded monomeric palladium(II) compounds containing the sugar-substituted thiourea as a monoanionic, O,S-chelate ligand, which was confirmed by an X-ray crystallographic study. Further studies of this class of complexes are continuing in our laboratories and will be reported in due time.

Experimental Part

General. All experiments were carried out under ambient conditions with no exclusion of air and moisture. The amino sugars **1a** and **1b** as well as the cyclopalladated nitrosamine $[Pd(O_2CMe)\{4\text{-}Me\text{–}C_6H_3\text{–}N(Me)NO\}]_2$ were prepared as described in [32][37][38]. $[Pd(O_2CMe)\{2\text{-}C_6H_4\text{–}C_8H_5N\text{–}4\text{-}COOMe\}]_2$ was prepared by treating palladium(II) acetate with commercial methyl 2-phenylquinoline-4-carboxylate in AcOH as described for the hexadecyl analogue [41]. All other chemicals and solvents were from commercial sources (*Acros Organics*, *Alfa Aesar*, or *Sigma–Aldrich*) and were used as received. Optical rotations: *Perkin–Elmer-241* polarimeter (10 cm, 1 ml cell); $[\alpha]_D^{25}$ determined at 589 nm (Na-D line). NMR Spectra: *Bruker-Avance-400* at 400 spectrometer; (^{1}H) and 101 MHz (^{13}C); δ in ppm rel. to Me_4Si as internal standard, J in Hz. Elemental analyses were performed by the staff of the microanalytical facility at the University of Wuppertal.

Single-Crystal X-Ray diffraction. Crystal diffraction data for **2a** and **2b** were collected at 150 K with an *Oxford-Diffraction-Gemini-E-Ultra* diffractometer, equipped with an *EOS-CCD* area detector and a four-circle kappa goniometer. For the data collection, the Mo-source emitting graphite-monochromated MoK_α radiation (λ 0.71073 Å) was used. Data integration, scaling, and empirical absorption corrections were carried out with the CrysAlis Pro program package [42]. Diffraction data for **4** were collected at 100 K with a *Bruker-APEX-II* diffractometer positioned in front of a *FR591* rotating Mo-anode equipped with focussing multilayer optics. The structures were solved with direct methods and refined by full-matrix-least-squares against F^2. The non-H-atoms were refined anisotropically, and H-atoms were placed at idealized positions and refined with the riding model. All calculations were carried out with the program Olex2 [43]. Important crystallographic data and refinement details are summarized in the *Table*[1]).

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[1]) CCDC-915384 (**2a**), -915384 (**2b**), and -915383 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

*Methyl 2-Deoxy-2-{[[(4-nitrobenzoyl)amino]thioxomethyl}amino}-β-*D*-glucopyranoside 3,4,6-Triacetate* (**2a**). To a soln. of KSCN (0.31 g, 3.13 mmol) in acetone (40 ml) was added 4-nitrobenzoyl chloride (0.58 g, 3.13 mmol), and the resulting mixture was heated to reflux for 1 h. Then the yellow suspension was cooled to r.t., a soln. of protected amino sugar **1a** (1.00 g, 3.13 mmol) in acetone (40 ml) was added, and the mixture was stirred for an additional 3 h at r.t. The almost colorless suspension was poured into 0.1M HCl (200 ml), and the resulting precipitate was isolated by filtration, washed with H_2O (200 ml), and dried in air: **2a** (1.22 g, 74%). Colorless solid. X-Ray-quality crystals were obtained by recrystallizing a sample from EtOH. $[\alpha]_D^{25} = +2.9$ ($c = 1$, CH_2Cl_2). ^{1}H-NMR (400 Hz, $CDCl_3$): 2.06, 2.07, 2.13 (*s*, 3 AcO); 3.55 (*s*, MeO); 3.79 (*m*, H–C(5)); 4.22 (*dd*, $J = 12.2$, 2.8, 1 H–C(6)); 4.33 (*dd*, $J = 12.2$, 4.7, 1 H–C(6)); 4.68 (*d*, H, $J = 7.9$, H–C(1)); 4.87 (*q*, $J = 8.8$, H–C(2)); 5.21 (*t*, $J = 9.2$, H–C(4)); 5.36 (*t*, $J = 9.4$, H–C(3)); 8.06 (*d*, H, $J = 8.8$, 2 arom. H); 8.38 (*d*, $J = 8.8$, 2 arom. H); 9.22 (*s*, C(O)NH); 10.74 (*d*, $J = 9.4$ Hz, C(S)NH). ^{13}C-NMR (101 MHz, $CDCl_3$): 20.61, 20.74 (Me); 57.02 (MeO); 58.86 (C(2)); 62.00 (C(6)); 68.09 (C(4)); 72.00 (C(5)); 72.54 (C(3)); 101.50 (C(1)); 124.18, 128.93 (arom. C); 136.90 (*C*C(O)); 150.68 (CNO_2); 164.71 (CO); 169.33, 170.54, 170.69 (Me*C*O); 180.91 (CS). Anal. calc. for $C_{21}H_{25}N_3O_{11}S$ (527.12): C 47.81, H 4.78, N 7.97, S 6.08; found: C 47.91, H 4.92, N 7.94, S 5.82.

*2-Deoxy-2-{[[(4-nitrobenzoyl)amino]thioxomethyl}amino}-β-*D*-glucopyranose 1,3,4,6-Tetraacetate* (**2b**). As described for **2a**, with KSCN (0.43 g, 4.40 mmol), 4-nitrobenzoyl chloride (0.82 g, 4.40 mmol), and amino sugar **1b** (1.53 g, 4.40 mmol): **2b** (1.81g, 74%). Colorless solid. $[\alpha]_D^{25} = +21.01$ ($c = 1$, CH_2Cl_2). ^{1}H-NMR (400 Hz, $CDCl_3$): 2.07, 2.09, 2.13, 2.15 (*s*, 4 AcO); 3.94 (*m*, H–C(5)); 4.19 (*dd*, $J = 12.3$, 2.6, 1 H–C(6)); 5.35 (*dd*, $J = 12.5$, 4.7, 1 H–C(6)); 5.08 (*q*, $J = 8.7$, H–C(2)); 5.24 (*t*, $J = 9.1$, H–C(4)); 5.39 (*t*, $J = 9.2$, H–C(3)); 5.96 (*d*, $J = 8.2$, H–C(1)); 8.07 (*d*, $J = 8.8$, 2 arom. H); 8.37 (*d*, $J = 8.8$, 2 arom. H); 9.24 (*s*, C(O)NH); 10.77 (*d*, $J = 9.3$, C(S)NH). ^{13}C-NMR (101 MHz, $CDCl_3$): 20.58; 20.67; 20.71; 21.00 (Me); 57.82 (C(2)); 61.64 (C(6)); 67.38 (C(4)); 72.11 (C(3)); 72.90 (C(5)); 92.12 (C(1)); 124.17, 128.99 (arom. C); 136.65 (*C*C(O)); 150.72 (CNO_2); 164.47 (CO); 169.14, 169.31, 170.35, 170.64 (Me*C*O); 181.24 (CS). Anal. calc. for $C_{22}H_{25}N_3O_{12}S \cdot EtOH$ (587.14): C 47.02, H 4.97, N 7.15, S 5.46; found: C 47.64, H 5.03, N 7.39, S 5.26.

*{Methyl 2-Deoxy-2-{[[(4-nitrobenzoyl-κO)amino](thioxo-κS)methyl}amino}-β-*D*-glucopyranosidato 1,3,4,6-tetraacetate}{2-[4-(methoxycarbonyl)quinolin-2-yl-κN]phenyl-κC}palladium* (**4**). A mixture of **2** (0.07 g, 0.134 mmol) and the palladacycle $[Pd(O_2CMe)\{2\text{-}C_6H_4\text{–}C_8H_5N\text{–}4\text{-}COO_2Me\}]_2$ (0.05 g, 0.061 mmol) in MeCN (20 ml) was heated to reflux for 30 min. The resulting yellow soln. was concentrated, and the residue was washed with H_2O and Et_2O and subsequently dried in air: **4** (0.48 g, 88%). Yellow solid. $[\alpha]_D^{25} = -105.6$ ($c = 1$, CH_2Cl_2). ^{1}H-NMR (400 Hz, $CDCl_3$)[2]): 2.10 (br. s, 9 H, Me); 3.56 (*s*, MeO–C(1)); 3.80 (*m*, H–C(5)); 4.11 (*s*, COOMe); 4.18 (*dd*, $J = 12.2$, 1.8, 1 H–C(6)); 4.36 (*dd*, $J = 12.5$, 4.8, 1 H–C(6)); 4.62 (*d*, $J = 7.8$, H–C(2)); 4.90 (*m*, H–C(1)); 5.33 (*m*, H–C(3), H–C(4)); 6.91 (*d*, $J = 9.3$, NH); 7.01 (*m*, H_c, H_b); 7.35 (*d*, $J = 7.6$, H_d); 7.54 (*d*, $J = 7.6$, H_a); 7.61 (*m*, H_f, H_g); 8.25 (*m*, 4 arom. H, $C_6H_4NO_2$); 8.65 (*d*, $J = 7.3$, H_h); 8.94 (*d*, $J = 7.1$, H_i); 9.07 (*d*, $J = 8.1$, H_e). Anal. calc. for $C_{38}H_{38}N_4O_{13}PdS$ (896,12): C 50.87, H 4.27, N 6.24, S 3.57; found: C 50.58, H 4.56, N 6.30, S 3.53.

*{Methyl 2-Deoxy-2-{[[(4-nitrobenzoyl-κO)amino](thioxo-κS)methyl}amino}-β-*D*-glucopyranosideato 1,3,4,6-tetraacetate}{5-methyl-2-[methyl(nitroso-κN)amino]phenyl-κC}palladium* (**3**): As described for **4**, with **2a** (0.09 g, 0.174 mmol) and palladacycle $[Pd(O_2CMe)\{4\text{-}Me\text{–}C_6H_3\text{–}N(Me)NO\}]_2$ (0.05 g, 0.079 mmol): **3** (0.41 g, 66%). Yellow solid. $[\alpha]_D^{25} = -67.6$ ($c = 1$, CH_2Cl_2). ^{1}H-NMR (400 Hz, $CDCl_3$)[2]): 2.04, 2.07, 2.13 (*s*, 3 Me); 2.22 (*s*, Me); 3.50 (*s*, MeO–C(1)); 3.60 (*s*, MeN); 3.79 (*m*, H–C(5)); 4.19 (*dd*, $J = 12.2$, 2.5, 1 H–C(6)); 4.36 (*dd*, $J = 12.5$, 5.0, 1 H–C(6)); 4.49 (*d*, $J = 7.9$, H–C(1)); 4.91 (*m*, H–C(2));

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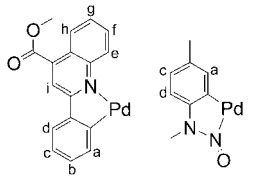
[2]) Atom numbering:



5.22 (q, $J = 9.7$, H–C(4)); 5.31 (m, H–C(3)); 6.72 (d, $J = 9.3$, NH); 6.84 (d, $J = 8.0$, H_d); 6.93 (dd, $J = 8.0$, 2.3, H_c); 7.05 (d, $J = 2.3$, H_a); 8.28 (d, $J = 8.8$, 2 arom. H of $C_6H_4NO_2$), 8.41 (d, $J = 8.8$ Hz, 2 arom. H of $C_6H_4NO_2$). Anal. calc. for $C_{29}H_{36}N_5O_{12}PdS$ (784.11): C 44.36, H 4.62, N 8.92, S 4.08; found: C 44.24, H 4.89, N 8.78, S 3.96.

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