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Inorganica Chimica Acta 361 (2008) 2731–2739
Inorganica Chimica Acta
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Linear homobimetallic 4-thioacetyl-substituted NCN pincer palladium(II) and platinum(II) complexes with *N*-bidentate connecting units (NCN = $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}R\text{-}4]^-$)

Katrin Döring [a], Deeb Taher [a], Bernhard Walfort [a], Martin Lutz [b], Anthony L. Spek [b], Gerard P.M. van Klink [c], Gerard van Koten [c], Heinrich Lang [a,*]

[a] *Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany*
[b] *Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, NL-3584 CH, Utrecht, The Netherlands*
[c] *Organic Synthesis and Catalysis, Debye Institute, Utrecht University, Padualaan 8, NL-3584 CH, Utrecht, The Netherlands*

Received 12 November 2007; accepted 26 January 2008
Available online 2 February 2008

Abstract

The synthesis and characterization of homobimetallic palladium and platinum complexes of type [(Me(O)CS-4-NCN–M ← N∩N → M–NCN-4-SC(O)Me]$(OTf)_2$ (Me(O)CS-4-NCN = $[C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}SC(O)Me\text{-}4]^-$; N∩N = 4,4′-bipyridine (bipy); M = Pd, **12**; M = Pt, **13**) is reported. The required bifunctional thio-acetyl NCN pincer starting compound NC(Br)N-4-SC(O)Me (**2**) has been synthesized by the consecutive reactions of NC(Br)N–I ($I\text{-}1\text{-}C_6H_2(CH_2NMe_2)_2\text{-}3,5\text{-}Br\text{-}4$) (**1**) with ^{t}BuLi, S_8 and Me(O)CCl, respectively. Chemoselective metallation at the C_{aryl}–Br bond was achieved by the reaction of **2** with the palladium(0) source $[Pd_2(dba)_3]$ (**3**) (dba = dibenzylidene acetone). Treatment of thus formed [Pd(NCN-4-SC(O)Me)(Br)] (**4**) with [AgOTf] (**8**) (OTf = triflate, OSO_2CF_3) gave [Pd(NCN-4-SC(O)Me)(H_2O)][OTf] (**9**) which was further reacted with 0.5 equiv. of 4,4′-bipyridine (**11a**) to afford rigid-rod structured **12**. When $[Pt(tol)_2(SEt_2)]_2$ (**5**) (tol = 4-tolyl) was used instead of **3**, then **13** was produced *via* the in situ formation of [PtBr(NCN-4-SC(O)Me)] (**7**) and [Pt(NCN-4-SC(O)Me)(H_2O)][OTf] (**10**). Another possibility to synthesize **7** relied upon the subsequent reaction of **1** with 0.5 equiv. of **5** to give [PtBr(NCN-4-I)] (**6**) which further reacted with ^{t}BuLi, 1/8 S_8 and Me(O)CCl to afford **7**. The cyclic voltammograms of **2**, **7**, and **13** are discussed.

Complex **7** was structurally characterized by single crystal X-ray crystallography. Organometallic **7** crystallizes with three independent molecules in the asymmetric unit and displays a monomeric structure as commonly encountered in d^8-metal pincer chemistry.

Keywords: Palladium; Platinum; NCN pincer; Thioacetyl; Homobimetallic; X-ray structure; Cyclic voltammetry

1. Introduction

Transition metal complexes featuring electron-rich and bulky pincer ligands, as the NCN building block (NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$) have found substantial applications in, *e.g.*, organic and organometallic synthesis and homogeneous catalysis [1]. In XCX pincer transition metal chemistry (X = N, P, O, S, ...) stable M–C bonds (M = Pd, Pt, ...) are present due to the additional bis-*ortho*-chelating effect of the *ortho*-amino substituents present in, for example, the mono-anionic NCN pincer ligand [2–5]. This opens the possibility to prepare *para*-functionalized complexes which can be used as "molecular tinkertoys" to prepare larger molecules with new functionalities [6]. If thiol or thio-acetyl end-grafted moieties are present such one-dimensional shaped molecules might be applied in the self-assembly on gold surfaces, or to span metal sur-

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[*] Corresponding author.
E-mail address: heinrich.lang@chemie.tu-chemnitz.de (H. Lang).

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doi:10.1016/j.ica.2008.01.023

faces/electrodes and hence, such single molecules may function as key components in future computational devices [7]. In this respect, attention was paid to nanoscale size organic thiols in recent years [8–15], due to their intrinsic semiconductor or insulator properties [16–26]. Next to organic thiols also organometallic systems are of considerable interest [26,27].

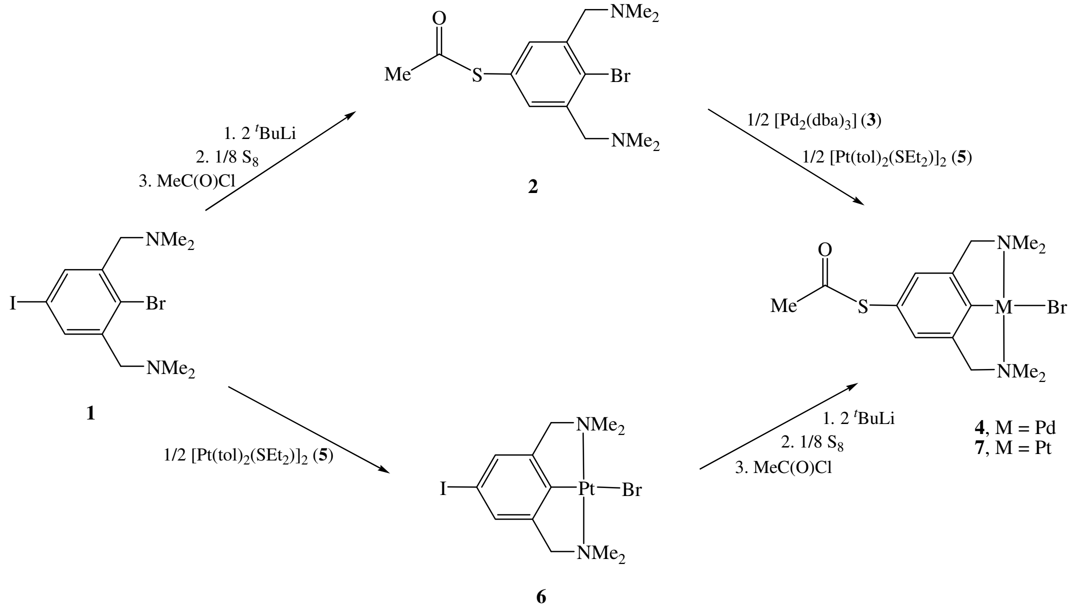
We here report on the synthesis, properties and characterization of linear thio-acetyl end-capped homobimetallic NCN–palladium and –platinum complexes.

2. Results and discussion

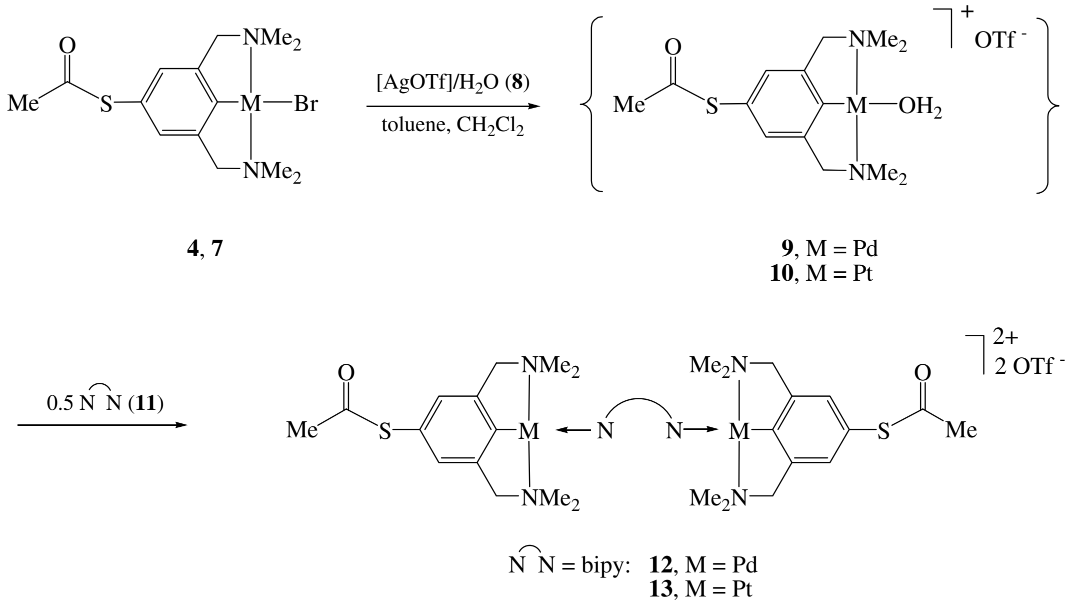
The synthesis of linear homobimetallic [*trans*-(Me(O)CS-4-NCN–M ← $N^{\cap}N$ → M–NCN-4-SC(O)Me](OTf)$_2$ (M = Pd, Pt; NCN = [$C_6H_2(CH_2NMe_2)_2$-2,6-SC(O)Me-4]$^-$; $N^{\cap}N$ = 4,4′-bipyridine (bipy)) (**12**, **13**) was attempted using different synthetic methods as outlined in Schemes 1 and 2.

As suitable starting material we chose NC(Br)N–I (NC(Br)N–I = I-1-$C_6H_2(CH_2NMe_2)_2$-3,5-Br-4) (**1**) [28a]. In this NCN pincer arene molecule two different halide–carbon$_{\text{aryl}}$ σ-bonds are available for the introduction of a thio-ester group. Due to the higher reactivity of C$_{\text{aryl}}$–I bonds over C$_{\text{aryl}}$–Br, selective metallation can be performed by making use of ^{t}BuLi. Lithium–iodide exchange is achieved at −100 °C by using 2 equiv. of ^{t}BuLi. Thus formed NC(Br)N–Li (**Li–1**) further reacts with sulfur and MeC(O)Cl to give the thio-acetyl NCN pincer arene molecule NC(Br)N-4-SC(O)Me (**2**) (Scheme 1) [28b]. Palladation of **2** with [$Pd_2(dba)_3$] (**3**) (dba = dibenzylidene acetone) as palladium source occurs in toluene at 25 °C. After appropriate work-up, dark brown [PdBr(NCN-4-SC(O)Me)] (**4**) could be isolated in 25% yield. Attempts to synthesize **4** by initial *trans*-metallation of the *para*-iodo palladium(II) complex [PdBr(NCN-4-I)] with ^{t}BuLi only resulted in the decomposition of the appropriate in situ generated species [28a]. The iso-structural NCN–platinum complex [PtBr(NCN-4-SC(O)Me)] (**7**) is available by using the same synthesis methodology as described for the preparation of **4**, however, instead of **3**, [Pt(tol)$_2$(SEt$_2$)]$_2$ (**5**) (tol = 4-tolyl) was used as platinum(0) source (Scheme 1) [28b]. Another possibility to prepare **7** is given by the oxidative addition of **1** to **5**, whereby [PtBr(NCN-4-I)] (**6**) is formed [28a], which further reacts in a consecutive reaction sequence with ^{t}BuLi, S_8 and MeC(O)Cl, respectively, to give the mononuclear NCN–platinum complex **7** in good yield (Scheme 1, Section 4) [28b].

Mononuclear **4** can successfully be used in the preparation of homobimetallic **12** (Scheme 2). Replacement of the Br substituent by the triflate anion, as a better leaving group, is possible by treatment of **4** with equimolar amounts of [AgOTf] (**8**) (TfO = triflate, OSO_2CF_3) in a toluene-dichloromethane mixture of ratio 5:2 at 25 °C, whereby [Pd(NCN-4-SC(O)Me)(H_2O)][OTf] (**9**) is formed as intermediate (Scheme 2). On addition of 0.5 equiv. of 4,4′-bipyridine (bipy) (**11**) to **9**, substitution of H_2O by the better π-acid **11** takes place and homobimetallic **12** is produced in excellent yield. However, it appeared that **12** is only stable at low temperature, while at room temperature it rapidly decomposes to give a insoluble black material. Exchange of the counter ion OTf$^-$ by, for example, BF_4^- or ClO_4^- did not produce a significantly more stable product. Thus, an analogous Pt–NCN pincer molecule was prepared. The synthesis protocol described for the preparation of **12** could successfully be transferred to synthesize iso-structural [*trans*-(Me(O)CS-4-NCN)Pt ← $N^{\cap}N$ → Pt(NCN-4-SC(O)-Me)](OTf)$_2$ (**13**, $N^{\cap}N$ = bipy) (Scheme 2, Section 4). A compound similar to **13** could recently be prepared and



Scheme 1. Synthesis of the 4-thioacetyl-substituted NCN pincer palladium(II) and platinum(II) complexes **4**, **6** and **7** [28].



Scheme 2. Synthesis of homobimetallic **12** and **13**.

characterized by single X-ray diffraction studies, *i.e.* [*trans*-(Me(O)CS-4-NCN)Pt ← $N^{\cap}N$ → Pt(NCN-4-SC(O)Me)]-$(OTf)_2$ (**14**, $N^{\cap}N = C_6H_4$-1,4-$(C{\equiv}N)_2$) [28b]. In the latter molecule two $[(MeC(O)S\text{-}4\text{-}NCN)Pt]^+$ moieties are connected by a linear C_6H_4-1,4-$(C{\equiv}N)_2$ unit to form a 2:1 coordination complex with an intramolecular platinum–platinum separation of 11.976(6) Å [28b].

Purification of **12** and **13** was possible by addition of *n*-pentane to dichloromethane solutions containing these complexes. By this procedure only the desired products precipitated due to their ionic character, while the impurities stay in the supernatant layer. No further purification is necessary, except washing of the residues with *n*-pentane.

After appropriate work-up, complexes **12** and **13** could be isolated as bright yellow solids which are only soluble in polar organic solvents such as tetrahydrofuran and dichloromethane [28b]. In acetonitrile, dimethylsulfide and dimethylformamide they decomposed even at low temperature. Decomposition was also observed on their exposure to air and moisture. The same behavior was observed for **4** and **7** [28b].

Specifically, all compounds have elemental analyses consistent with their respective compositions. Multinuclear NMR studies, along with internal consistency in the spectral data among the diverse species, anchored to X-ray crystal structure determinations (**7**) unambiguously established their structures.

In particular, the IR spectra of **2**, **4**, **7**, **12** and **13** show one characteristic stretching vibration for the carbonyl groups at ca. 1700 cm^{-1}. The triflate ion in **12** and **13** gave rise to one very characteristic absorption at ca. 1265 cm^{-1} (ν_{SO}) which is consistent with the *non*-coordinating character of this group [27,29].

The NMR data (^1H, $^{13}C\{^1H\}$) of all complexes agree with the structures proposed (vide supra and Section 4).

As typical, the proton signals for the Me_2NCH_2 NCN units are shifted to lower field upon their coordination to palladium (complexes **4** and **12**) or platinum (complexes **7** and **13**) [28b,30]. The coordinated bipy connecting unit in **12** and **13** displays two signals in the ^1H NMR spectra as required for these molecules. Evidence for the chemoselective platinum insertion into the C_{aryl}–Br bond in **2** and hence, formation of **7** is accompanied by a pair of doublets centered around the major peaks for the Me_2NCH_2 NCN pincer units due to additional spin–spin coupling to platinum ($^3J_{PtH} = 35$–40 Hz) [28b,31].

The $^{13}C\{^1H\}$ NMR spectra of **2**, **4** and **7** show well-resolved signals typical for the organic groups present and confirm the proposed structures (Section 4) [28b]. For bimetallic **12** and **13** no ^{13}C NMR measurements could be carried out because these systems decompose in common organic solvents (vide supra).

Unequivocal confirmation of the proposed connectivity pattern was obtained from single crystal structure determination of **7**. Single crystals of **7** could be grown from slow diffusion of *n*-pentane into a dichloromethane solution containing **7** at room temperature.

The molecular structure of **7** is shown in Fig. 1. There are three independent molecules with comparable bond lengths and angles in the asymmetric unit. The major difference between the three molecules is the conformation of the thioacetyl substituent. Selected bond distances (Å), bond angles (°), and torsion angles (°) are summarized in Table 1. Crystallographic and refinement data are given in Section 4.

Molecule **7** displays a monomeric structure as normally encountered in d^8-metal NCN pincer chemistry (Fig. 1) [32]. Both five-membered metallacycles (Pt1, N11, C17, C12, C11 and Pt1, N12, C11, C16, C110) are puckered in the same direction corresponding to a local C_s symmetry

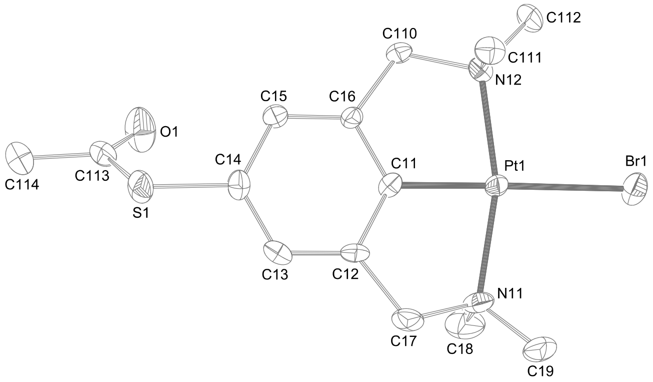


Fig. 1. ORTEP diagram of **7** in the crystal (50% probability level). Only one of three independent molecules is shown. Hydrogen atoms and dichloromethane solvent molecules are omitted for clarity.

Table 1
Selected bond distances (Å), bond angles (°), and torsion angles (°) for the three independent molecules of **7**[a]

	$x = 1$	$x = 2$	$x = 3$
Bond distances			
Pt*x*–Br*x*	2.5497(9)	2.5370(10)	2.5351(9)
Pt*x*–N*x*1	2.101(7)	2.087(6)	2.084(7)
Pt*x*–N*x*2	2.095(7)	2.084(7)	2.092(8)
Pt*x*–C*x*1	1.927(7)	1.905(8)	1.918(8)
S*x*–C*x*4	1.773(8)	1.774(10)	1.771(9)
Bond angles			
N*x*1–Pt*x*–N*x*2	162.8(3)	164.1(3)	164.5(3)
Br*x*–Pt*x*–C*x*1	175.9(2)	177.8(2)	177.1(3)
Br*x*–Pt*x*–N*x*1	95.75(19)	97.32(19)	96.86(19)
Br*x*–Pt*x*–N*x*2	100.44(18)	98.6(2)	98.6(2)
C*x*4–S*x*–C*x*13	102.4(4)	102.9(5)	104.2(5)
Torsion angles			
Pt*x*–C*x*1–C*x*2–C*x*3	−176.7(6)	−178.3(7)	173.2(6)
Pt*x*–C*x*1–C*x*6–C*x*5	178.6(6)	−179.4(7)	−176.4(7)
N*x*1–C*x*7–C*x*2–C*x*1	−22.9(10)	−25.9(10)	22.7(10)
N*x*2–C*x*10–C*x*6–C*x*1	−25.0(10)	−22.4(10)	22.2(11)
C*x*4–S*x*–C*x*13–C*x*14	174.1(7)	179.5(8)	−175.6(9)
C*x*3–C*x*4–S*x*–C*x*13	−118.4(7)	−91.3(8)	−73.9(9)
C*x*5–C*x*4–S*x*–C*x*13	62.5(8)	91.6(9)	111.5(9)

[a] Standard uncertainties of the last significant digit(s) are shown in parentheses.

perpendicular to the phenyl plane. Consequently, the torsion angles in the five-membered chelate rings have the same signs within one molecule and approximately the same magnitude. To accommodate this puckering, the planar phenyl rings are rotated slightly about the Pt–C bonds forming dihedral angles of 13.5(3)°, 9.7(4)°, and 10.4(3)° with the Pt coordination planes of the three independent molecules. These twist angles are somewhat similar to the ones observed of other platinum complexes with related NCN ligands [33,34], except [PtI(NCN-4-Me)], which exhibits a dihedral angle of 9.5° [33b]. Similarly, the Pt–N distances for **7** (2.084(7)–2.101(7) Å, Table 1) are as expected for complexes with this type of chelating ligand [33,34]. The N–Pt–N angles of 162.8(3)–164.5(3)° substantially deviates from ideal *trans*-coordination. The deviation of this bond angle from 180° in related complexes has been attributed to the geometric preferences of the two five-membered chelate rings [34c,34d].

To preliminary investigate the electrochemical behavior of the above discussed complexes, exemplary the cyclic voltammograms of **2**, **7**, **13**, and [*trans*-(Me(O)CS-4-NCN)Pt ← $\mathrm{N}^{\cap}\mathrm{N}$ → Pt(NCN-4-SC(O)Me)](OTf)$_2$ (**14**, $\mathrm{N}^{\cap}\mathrm{N}$ = C_6H_4-1,4-(C≡N)$_2$) for comparison were recorded.

The cyclic voltammogram of the NCN pincer thioacetyl molecule **2** in dichloromethane possesses two irreversible oxidation peaks at $E_{\mathrm{p,ox}} = +0.62$ and $+1.00$ V. Most likely, the first oxidation peak is originating from the NCN pincer oxidation [9]. For benzyl amine an analogous behavior has been reported [35]. The second oxidation at $E_{\mathrm{p,ox}} = 1.00$ V presumably relates to the thio-acetyl moiety since similar irreversible peaks have been found for other Me(O)CS-containing organic compounds, *i.e.* I-1-C_6H_4-4-SC(O)Me and Me(O)CS-4-C_6H_4–C_6H_4-4′-SC(O)Me [27,36]. A reduction at $E_{\mathrm{p,red}} = -0.94$ V only occurs after oxidation of **2** lasting in multicyclic experiments. This clearly illustrates that this peak relates to an oxidized form of **2**. Analogous observations were made with similar thio-acetyl benzene and biarene molecules [27,36]. As expected, this peak is not observed, when the cyclic voltammetric measurements where firstly conducted into the cationic region.

Oxidative addition of the C–Br bond in **2** to platinum(0) results in the formation of mononuclear [PtBr(NCN-4-SC(O)Me)] (**7**) which exhibits irreversible oxidation peaks at $E_{\mathrm{p,ox}} = +0.49$, $+0.67$ and $+1.19$ V. In addition to these oxidations also an irreversible reduction peak at $E_{\mathrm{p,red}} = -0.73$ V is found, *i.e.* no re-oxidation peak is observed. The electro-oxidation of the platinum ion at +0.67 V is similar to that observed for [PtCl(NCN-4-Me)] ($E_{\mathrm{p,ox}} = +0.76$ V) [37]. This shows that the electron density at platinum in **7** has somewhat increased and hence, is more easier to oxidize [37]. This behavior is characteristic for the metal-centered oxidation of platinum(II) complexes resulting in a larger reorganization [38]. Similar irreversible waves have been reported for related metal complexes with NCN pincer ligands [37,39]. However, the electrochemical behavior of these compounds differs from other nearly reversible cooperative two-electron reagents, *i.e.* [Pt(pip$_2$NCN) (2,2′:6′,2″-terpyridine)]$^+$ [40]. The irreversible reduction peak at $E_{\mathrm{p,red}} = -0.73$ V is characteristic for thio-acetyl NCN pincer ligands and only occurs from an oxidized form of this unit (vide supra) [27,36].

The cyclic voltammograms of **13** and **14** display as observed before for **7**, irreversible oxidations at $E_{\mathrm{p,ox}} = +0.64$, $+0.89$ and $+1.20$ V for **13** and $E_{\mathrm{p,ox}} = +0.68$ and $+1.04$ V for **14**, whereby the waves for the platinum oxidation possess a somewhat more negative value than [PtBr(NCN-4-S(O)Me)] (**7**) indicating that the platinum atom becomes more electron poor due to the π-acceptor nature of the Lewis-base $\mathrm{N}^{\cap}\mathrm{N}$ [28b]. Previously, a similar behavior has been noted for related palladium compounds [34]. This shows that these complexes are insulators rather than conductors [40], which is consistent with the similar electron-donating ability for neutral donor ligands with reference to electrochemical studies on other related homobimetallic platinum(II) complexes [34,39]. In addition, the cyclic voltammogram of **13** displays two chemically reversible reduction waves at $E_0 = -1.15$ ($\Delta E_p = 200$ mV) and $E_0 = -1.39$ V ($\Delta E_p = 140$ mV). A similar behavior has been noted for related compounds [39,41]. The two waves can be assigned to one-electron reductions of the bipy ligand (for comparison, free bipy shows a reduction process at $E_0 = -2.76$ V with $\Delta E_p = 340$ mV) [42]. This implies a decreased charge density at the bipy ligand and hence, a more easier reduction. A similar behavior was already observed for other 4,4′-bipy bridged transition metal complexes [42].

Complex **14** gave a cyclic voltammogram with relevant electrode potentials at $E_{p,ox} = +0.68$ and $+1.04$ V and at $E_{p,red} = -0.72$, -1.32 and -1.58 V [28b]. The oxidation peaks correspond to the irreversible oxidation of the platinum atoms, the NCN and thio-acetyl units, while the potentials in the negative region result from the reduction of an oxidized NCN thio-acetyl (vide supra) and the connecting unit C_6H_4-1,4-($C{\equiv}N$)$_2$ (for comparison, free terephthalonitrile possesses two reduction peaks at $E_0 = -2.23$ V ($\Delta E_p = 350$ mV) and $E_0 = -2.70$ ($\Delta E_p = 300$ mV) [42]. This points to a significant shift of the ligand centered reductions upon coordination to *para*-thioacetyl NCN pincer platinum cations as discussed earlier for **13** [43,44].

3. Conclusion

Cationic homobimetallic linear thio-acetyl end-grafted NCN–palladium and NCN–platinum complexes (NCN = [4-thioacetyl-$C_6H_2(CH_2NMe_2)_2$-2,6]$^-$) with a 4,4′-bipyridine connecting unit between the appropriate transition metal atoms have been synthesized in a straightforward way by using different synthesis methodologies. Chemoselective metallation at the C_{aryl}–Br bond in NC(Br)N-4-SC(O)Me was achieved by using [$Pd_2(dba)_3$] and [$Pt(tol)_2(SEt_2)]_2$, respectively, as precursor compounds. Complexes [MBr(NCN-4-SC(O)Me)] (M = Pd, Pt) are thereby obtained in good yield under mild conditions. Subsequent reaction of the latter species with [AgOTf] followed by addition of 4,4′-bipyridine gave the 2:1 homobimetallic palladium and platinum complexes of structural type [*trans*-(MeC(O)S-4-NCN)M ← N$^\frown$N → M(NCN-4-SC(O)-Me)](OTf)$_2$ (M = Pd, Pt) in which the transition metals are connected by the linear π-conjugated nitrogen-containing bridging unit bipy (N$^\frown$N) as evidenced by single X-ray structure determination of [*trans*-(Me(O)CS-4-NCN)Pt–N≡C-C_6H_4–C≡N–Pt(NCN-4-SC(O)Me)](OTf)$_2$ [28b]. While the homobimetallic palladium complex rapidly decomposes even at low temperature, the respective platinum assembly is fairly stable. The homobimetallic palladium and platinum complexes are insulators. Similar observations were made with the electron-donating cability of neutral donor ligands with reference to electrochemical studies on other related homobimetallic palladium and platinum(II) complexes.

4. Experimental

4.1. General methods

All reactions were carried out in an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen, Germany; H_2O traces: molecular sieve, 4 Å, Roth company) using standard Schlenk techniques. Solvents were purified by distillation (*n*-hexane and dichloromethane: calcium hydride; benzene and toluene: sodium; tetrahydrofuran: sodium/benzophenone ketyl). FT-IR spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer (KBr or as film between NaCl plates). NMR spectra were recorded with a Bruker Avance 250 spectrometer operating in the Fourier transform mode. ^{1}H NMR spectra were recorded at 250.123 MHz (internal standard, relative to $CDCl_3$, δ 7.26 and CD_2Cl_2, δ 5.32). $^{13}C\{^1H\}$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to $CDCl_3$, δ 77.16 and CD_2Cl_2, δ 53.50); $^{31}P\{^1H\}$ NMR were recorded at 101.202 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ 139.0, relative to 85% H_3PO_4, δ 0.00). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane with the solvent signal as reference. Cyclic voltammograms were recorded in a dried cell, purged with purified argon at 25 °C. Platinum wires served as working and as counter electrode. A Ag/AgCl electrode served as reference electrode. For ease of comparison, all potentials are converted using the redox potential of the ferrocene-ferrocenium couple FcH/FcH$^+$ (FcH = $(\eta^5\text{-}C_5H_5)_2Fe$) as the reference ($E_0 = 0.00$ V, $\Delta E_p = 125$ mV) [47,48]. Electrolyte solutions were prepared from freshly distilled tetrahydrofuran and [n-Bu_4N]PF_6 (dried in *oil-pump vacuum* at 120 °C). The appropriate organometallic complexes were added at $c = 1.0$ mM. The cyclic voltammograms were recorded at a scan rate of 200 mV s^{-1} using a Princeton Applied Research EG&G 263A analyzer. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries with a Gallenkamp MFB 595 010 melting point apparatus. Microanalyses were performed by the Organic Department at Chemnitz, University of Technology and the Institute of Organic Chemistry at the University of Heidelberg.

4.2. General remarks

I-1-$C_6H_2(CH_2NMe_2)_2$-3,5-4-Br (**1**) [28a], [$Pd_2(dba)_3$] (**3**) [45], [PdBr(NCN-4-I)] [28a], [$Pt(tol)_2(SEt_2)]_2$ (**5**) [46] and [PtBr(NCN-4-I)] (**6**) [28a] were prepared by published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

4.3. Synthesis of 2

Compound **1** (1.0 g, 2.52 mmol) was dissolved in tetrahydrofuran (300 mL) and ^{t}BuLi (3.40 mL, 5.04 mmol, 1.5 M in *n*-pentane) was drop-wise added at −100 °C during

10 min. After stirring the reaction mixture for 10 min at this temperature, sulfur (0.08 g, 2.52 mmol) dissolved in 50 mL of tetrahydrofuran was slowly added. The reaction mixture was allowed to warm to 0 °C and was stirred for 45 min at this temperature. Afterward, the solution was again cooled to −100 °C and acetyl chloride (0.20 g, 2.52 mmol) was added in a single portion. The reaction solution was allowed to warm to room temperature overnight. Water (5 mL) was added and the reaction mixture was extracted with dichloromethane (3 × 25 mL). The combined layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by chromatography (column size: 20 × 2.5 cm; Silica gel; *n*-hexane–dichloromethane, ratio of 10:3, 3% Et_3N). The solvents were removed from the eluate in *oil-pump vacuum* to leave a yellow oil. Yield: 0.56 g (1.64 mmol, 65% based on **1**).

Anal. Calc. for $C_{14}H_{21}BrN_2OS$ (345.30): C, 48.70; H, 6.13; N, 8.11. Found: C, 48.89; H, 6.14; N, 8.31%. IR (NaCl): 2940 (m), 2855 (m). 2771 (m), 1708 (vs) (ν_{CO}), 1644 (m), 1570 (w), 1455 (s), 1421 (m), 1353 (s), 1260 (s), 1218 (s), 1173 (s), 1148 (w), 1112 (vs), 1097 (sh), 1142 (sh), 1119 (vs), 948 (s), 909 (w), 853 (m), 887 (m), 838 (m), 802 (s), 730 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.3$ (s, 12H, $N(CH_3)_2$), 2.3 (s, 3H, CH_3), 3.5 (s, 4H, CH_2), 7.4 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.4$ (CH_3), 45.7 ($N(CH_3)_2$), 63.9 (CH_2), 126.9 ($^iC/C_6H_2$), 128.3 ($^iC/C_6H_2$), 134.9 (C_6H_2), 140.0 ($^iC/C_6H_2$), 193.7 (CO). HRMS calcd. for $C_{14}H_{22}N_2BrOS$: (M^+) 345.0423, found: 345.0465.

4.4. Synthesis of **4**

Compound **2** (0.7 g, 2.02 mmol) was dissolved in 80 mL of toluene and $[Pd_2(dba)_3]$ (**3**) (1.16 g, 2.02 mmol) was added in a single portion at 25 °C. After 4 h of stirring at this temperature, all volatiles were removed in *oil-pump vacuum* and the residue was dissolved in dichloromethane (5 mL). *n*-Hexane (60 mL) was added, whereby a brown solid precipitated. The supernatant layer was decanted and the residue was washed twice with *n*-hexane (20 mL) to give **4** as a brown solid (0.22 g, 0.50 mmol, 25% based on **2**).

M.p.: 80 °C (dec.). *Anal.* Calc. for $C_{14}H_{21}BrN_2OPdS.CH_2Cl_2$ (536.65): C, 33.57; H, 4.32; N, 5.22. Found: C, 33.80; H, 4.37; N, 5.14%. IR (KBr): 2970 (m), 2911 (s), 1697 (s) (ν_{CO}), 1620 (sh), 1452 (s), 1432 (sh), 1335 (m), 1268 (w), 1192 (m), 1104 (vs), 1050 (m), 1017 (s), 957 (s), 863 (s), 838 (s), 769 (w), 728 (w), 699 (m), 619 (s), 521 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.4$ (s, 3H, CH_3), 2.9 (s, 12H, $N(CH_3)_2$), 4.0 (s, 4H, CH_2), 6.8 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.2$ (CH_3), 53.9 ($N(CH_3)_2$), 74.4 (CH_2), 123.4 ($^iC/C_6H_2$), 126.0 ($^iC/C_6H_2$), 128.5 (C_6H_2), 146.1 ($^iC/C_6H_2$), 194.9 (CO). MALDI-TOF MS: *m/z* 371.0 $[M-Br]^+$.

4.5. Synthesis of **7**

Method A: Compound **2** (0.34 g, 0.99 mmol) was dissolved in 80 mL of benzene and 0.5 equiv. of **5** (0.46 g, 0.999 mmol) were added in a single portion at 25 °C. After 4 h of refluxing, all volatiles were removed in *oil-pump vacuum* and the residue was dissolved in dichloromethane (5 mL). By addition of 60 mL of *n*-hexane a brown precipitate formed. The supernatant solution was removed by canula, the yellow solid was washed twice with *n*-pentane (10 mL), and the residue was dried in *oil-pump vacuum* for 4 h. Yield: 0.42 g (0.79 mmol, 80% based on **2**).

Method B: Compound **6** (0.60 g, 0.89 mmol) was dissolved in tetrahydrofuran (100 mL) and ^{t}BuLi (1.18 mL, 1.78 mmol, 1.5 M in *n*-pentane) was added at −100 °C during 5 min. After stirring the reaction mixture at this temperature for additional 5 min, sulfur (0.03 g, 0.89 mmol) dissolved in tetrahydrofuran (20 mL) was slowly added. Stirring was continued for additional 15 min at this temperature and then acetyl chloride (0.07 g, 0.89 mmol) was added. The thus obtained reaction mixture was allowed to warm to room temperature during 4 h. All volatiles were removed in *oil-pump vacuum* and the residue was dissolved in toluene-dichloromethane (ratio 5:2) (10 mL). The reaction mixture was filtered through a pad of Celite. *n*-Hexane (60 mL) was added, whereby a yellow solid precipitated. The supernatant solution was removed by canula and the residue was washed twice with *n*-hexane (20 mL) to gave **7** as a yellow solid (0.23 g, 0.42 mmol, 50% based on **6**).

M.p.: 90 °C (dec.). *Anal.* Calc. for $C_{14}H_{21}BrN_2OPtS$ (540.38): C, 31.12; H, 3.92; N, 5.18. Found: C, 31.16; H, 3.83; N, 4.88%. IR (KBr): 2965 (m), 2912 (m), 1695 (s) (ν_{CO}), 1648 (s), 1621 (s), 1569 (m), 1465 (s), 1451 (s), 1429 (s), 1355 (m), 1338 (m), 1261 (m), 1233 (m), 1178 (sh), 1119 (s), 1099 (vs), 1051 (s), 1017 (s), 980 (s), 956 (s), 980 (s), 956 (s), 857 (m), 837 (s), 801 (m), 769 (m), 697 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.3$ (s, 3H, CH_3), 3.0 (t, 12H, $^3J_{PtH} = 38.7$ Hz, $N(CH_3)_2$), 4.1 (t, 4H, $^3J_{PtH} = 46.2$ Hz, CH_2), 6.8 (s, 2H, C_6H_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.1$ (CH_3), 55.3 ($N(CH_3)_2$), 76.8 (CH_2), 109.5 (C_6H_2), 125.8 (C_6H_2), 144.6 (C_6H_2), 157.9 (C_6H_2), 177.8 (CO).

4.6. X-ray crystal structure determination of **7**

$C_{14}H_{21}BrN_2OPtS \cdot 1/3(CH_2Cl_2)$, Formula weight = 568.70, yellowish plate, $0.48 \times 0.24 \times 0.06$ mm^3, monoclinic, $P2_1/c$ (no. 14), $a = 10.9569(15)$, $b = 45.982(5)$, $c = 11.3898(10)$ Å, $\beta = 110.332(8)°$, $V = 5380.9(10)$ Å^3, $Z = 12$, $D_x = 2.106$ g/cm^3, $\mu = 10.27$ mm^{-1}. X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.59$ Å^{-1} at a temperature of 150 K. 33,916 Reflections were integrated using the EvalCCD software [49]. An analytical absorption correction was applied (0.08–0.67 correction range) [50]. 9086 reflections were unique ($R_{int} = 0.0635$). The structure was solved with automated Patterson methods [51] and refined with SHELXL-97 [52a,52b] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in geometrically idealized positions and refined with a riding model. 583 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0413/0.0977. R_1/wR_2 [all refl.]: 0.0559/0.1050. $S = 1.092$. Residual electron density between −2.44 and 1.91 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program [50].

4.7. Synthesis of **12**

[AgOTf] (**8**) (85 mg, 0.33 mmol) was added in a single portion to **4** (150 mg, 0.33 mmol), which was dissolved in toluene-dichloromethane of ratio 5:2 (40 mL) at 25 °C. After 30 min of stirring, the reaction mixture was filtered through a pad of Celite. To this solution 4,4′-bipyridine (**11**) (24 mg, 0.165 mmol) was added and the resulting suspension was stirred for 30 min. By addition of 60 mL of *n*-hexane a brown precipitate formed. The supernatant solution was removed by filtration and the brown residue was dried in *oil-pump vacuum*. Yield: 131 mg (0.108 mmol, 65% based on **7**).

M.p.: 65 °C (dec.). IR (KBr): 3101 (m), 2926 (m), 1700 (s) (ν_{CO}), 1609 (s), 1532 (w), 1463 (s), 1415 (sh), 1264 (vs) ($\nu_{s(SO)}$), 1223 (m), 1155 (s), 1094 (sh), 1061 (m), 1030 (s) (ν_{CF}), 945 (m), 871 (w), 818 (s), 709 (w), 638 (s), 574 (m), 517 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 2.4$ (s, 6H, CH_3), 2.9 (bs, 24H, $N(CH_3)_2$), 4.2 (t, 8H, $^3J_{PtH} = 46.4$ Hz, CH_2), 7.1 (s, 4H, C_6H_2), 8.8 (bs, 4H, ^{o}H, C_6H_4N), 9.1 (bs, 4H, ^{m}H, C_6H_4N). $^{13}C\{^1H\}$ NMR data and elemental analysis could not be obtained, due to the high instability of **12**.

4.8. Synthesis of **13**

[AgOTf] (**8**) (73 mg, 0.28 mmol) was added in a single portion to **7** (153 mg, 0.28 mmol) which was dissolved in a mixture of toluene and dichloromethane of ratio 5:2 (40 mL) at 25 °C. After 30 min of stirring, the reaction mixture was filtered through a pad of Celite. To the eluate was added 4,4′-bipyridine (**11**) (22 mg, 0.14 mmol) and the resulting suspension was stirred until a clear solution was formed (30 min). Addition of 60 mL of *n*-hexane produced a yellow precipitate. The supernatant solution was decanted and the obtained yellow solid was dried in *oil-pump vacuum*. Yield: 136 mg (0.099 mmol, 75% based on **7**).

M.p.: 107 °C (dec.). *Anal.* Calc. for $C_{40}H_{50}F_6N_6O_8Pt_2S_4$ (1375.27): C, 34.93; H, 3.66; N, 6.11. Found: C, 34.67; H, 4.14; N, 6.45%. IR (KBr): 3101 (m), 2926 (m), 1700 (s) (ν_{CO}), 1609 (s), 1532 (w), 1463 (s), 1415 (sh), 1264 (vs) ($\nu_{s(SO)}$), 1223 (m), 1155 (s), 1094 (sh), 1061 (m), 1030 (s) (ν_{CF}), 945 (m), 871 (w), 818 (s), 709 (w), 638 (s), 574 (m), 517 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): $\delta = 2.4$ (s, 6H, CH_3), 2.9 (bs, 24H, $N(CH_3)_2$), 4.2 (t, 8H, $^3J_{PtH} = 46.4$ Hz CH_2), 7.1 (s, 4H, C_6H_2), 8.8 (bs, 4H, ^{o}H, bipy), 9.1 (bs, 4H, ^{m}H, bipy). $^{13}C\{^1H\}$ NMR data could not be obtained, due to the low solubility of **13** in common organic solvents.

5. Supplementary material

CCDC 659837 contains the supplementary crystallographic data for **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. This work was partially supported (M.L., A.L.S.) by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW).

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