Complexes with S-Donor Ligands, 4[◇]

Mono- and Di-Homo- and -Hetero-Nuclear Gold(I), Silver(I), and Palladium(II) Complexes with 2-(Methylthio)pyridine, Pyridine-2(1*H*)-thione, and Benzoxazole-2(3*H*)-thione. Some Examples of the Use of Complexes as Ligands

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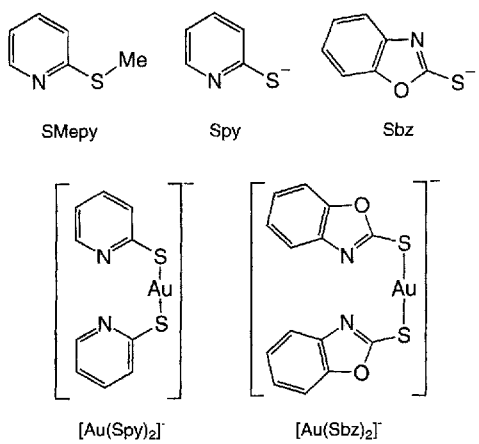
$AgClO_4$ reacts with bidentate ligands 2-(methylthio)pyridine (SMepy) or complexes PPN[Au(Spy)$_2$] [PPN = N(PPh$_3$)$_2$, HSpy = pyridine-2(1*H*)-thione) or PPN[Au(Sbz)$_2$] (HSbz = benzoxazole-2(3*H*)-thione), themselves acting as ligands, to give dinuclear complexes [Ag$_2$(μ-SMepy)$_2$](ClO$_4$)$_2$ (**1**), [AgAu(μ-Spy)$_2$] (**2**), or [AgAu(μ-Sbz)$_2$] (**3**), respectively. By treating **1** with [AuCl(tht)] (tht = tetrahydrothiophene), [Au(SMepy)(tht)]ClO$_4$ (**4**) is obtained which, in turn, reacts with SMepy to give [Au(SMepy)$_2$]ClO$_4$ (**5**). Similarly, [PdCl$_2$(NCPh)$_2$] reacts with SMepy in 1:1 molar ratio to give [Pd$_2$Cl$_2$(μ-Cl)$_2$(SMepy)$_2$] (**6**) which reacts with SMepy in 1:2 molar ratio to give [PdCl$_2$(SMepy)$_2$] (**7**). On the other hand, HSpy reacts with Ag_2CO_3 to give [Ag$_2$(μ-Spy)$_2$] (**8**), and (SMepyH)ClO$_4$ reacts with [Au(acac)PPh$_3$] (acacH = acetylacetone) to give [Au(SMepy)PPh$_3$]ClO$_4$ (**9**).

Interest in the study of thiolato complexes is based both on their use as models for the structure, bonding, and reactivity of metallo enzymes and on the structural diversity they display[1]. Heterocyclic thiolato complexes have found interesting applications in analysis, manufacture of polymers, medicine, or industry[2]. In particular, thiolatogold(I) complexes, such as the commercial antiarthritics myocrisin, allochrysine, solganol, or auranofin, are among the most important antiarthritic compounds[2b,c,g]. In addition, solganol has in vitro inhibitory effects on Human Inmunodeficiency Virus 1, which is the etiologic agent of AIDS[2h], and auranofin was found to be highly cytotoxic to tumour cells[2i] and active against i.p. P388 leukemia[2j].

Furthermore, 2-pyridinethionato and related ligands can coordinate up to three metal centers at short distances, thus offering the possibility of studying attractive metal-metal interactions, which for d^{10} systems have attracted considerable attention[3]. We have found[3a] that 2-pyridyl-substituted phosphorus ylides, in which the NCC skeleton is similar to that of the NCS moiety present in the systems here described, can lead to loose $[Au_3]^{3+}$, $[Au_2Ag]^{3+}$, and $[Au_2Cu]^{3+}$ clusters displaying short Au···Au, Au···Ag, or Au···Cu contacts.

In this paper we report on the synthesis and characterization of new mono- and dinuclear complexes of gold(I), silver(I), and palladium(II) derived from 2-(methylthio)pyridine (SMepy), pyridine-2(1*H*)-thione (HSpy), benzoxazole-2(3*H*)-thione (HSbz) (see Scheme 1), for which few percedents are known[4,5]. As far as we are aware, only one Rh(I) complex containing 2-(methylthio)pyridine has been reported, but was not isolated[6]. We have previously described the synthesis of anionic bis(thiolato)gold(I) complexes of the type $[Au(SR)_2]^-$[4], two of which, namely $[Au(Spy)_2]^-$ and $[Au(Sbz)_2]^-$ (see Scheme 1), are here used as ligands for the synthesis of heterodinuclear complexes.

Scheme 1



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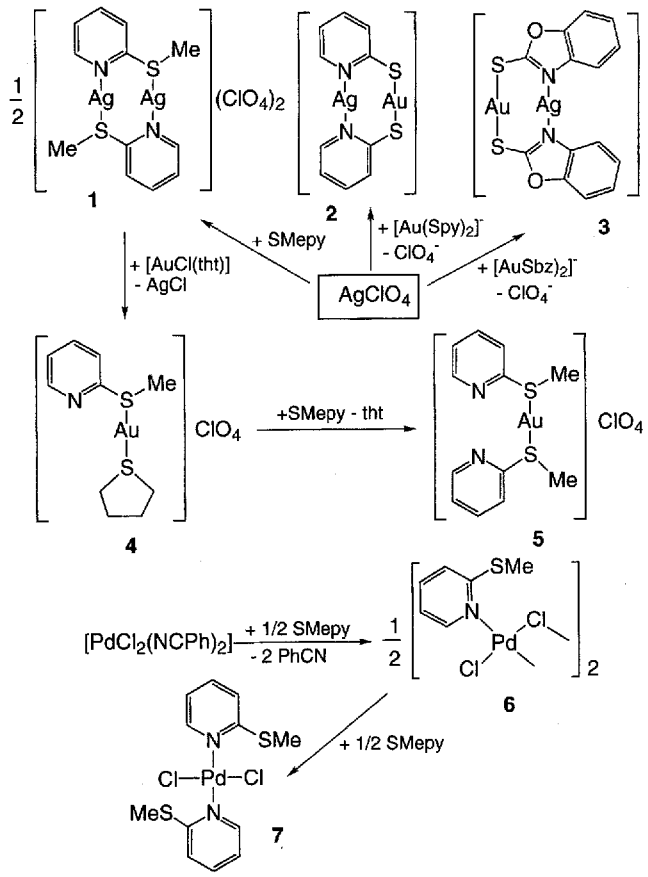
Results and Discussion

The synthesis of complexes was achieved by substitution or acid-base reactions. Thus, when $AgClO_4$ was treated in acetone with the bidentate ligands 2-(methylthio)pyridine (SMepy), PPN[Au(Spy)$_2$] [PPN = N(PPh$_3$)$_2$, HSpy = pyridine-2(1*H*)-thione] or PPN[Au(Sbz)$_2$] [HSbz = benzoxazole-2(3*H*)-thione] in 1:1 molar ratio the complexes [Ag$_2$(μ-SMepy)$_2$](ClO$_4$)$_2$ (**1**), [AgAu(μ-Spy)$_2$] (**2**), or [AgAu(μ-Sbz)$_2$] (**3**), respectively were obtained in high yields (see Scheme 2). Complex **1** is soluble in acetone and was precipitated with diethyl ether, whereas **2** and **3** precipitate in acetone, thus allowing separation of the byproduct PPN(ClO$_4$). Complex **1** reacts in dichloromethane with [AuCl(tht)] (2:1) (tht = tetrahydrothiophene) to give AgCl and a solution from which complex [Au(SMepy)(tht)]ClO$_4$ (**4**) was isolated upon addition of diethyl ether. The labile tht ligand present in **4** can be replaced by the ligand SMepy to give [Au(SMepy)$_2$]ClO$_4$ (**5**).

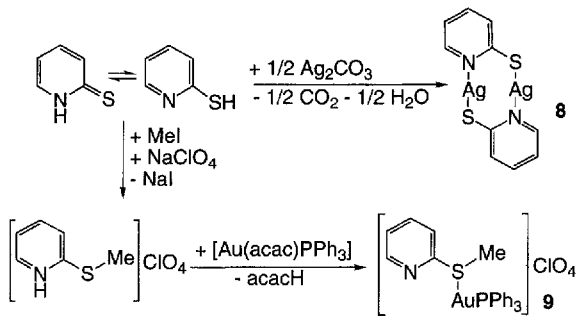
Scheme 2



The ligand SMepy reacts with [PdCl$_2$(NCMe)$_2$] (1:1) in acetone to give the insoluble complex [Pd$_2$Cl$_2$(μ-Cl)$_2$(SMepy)$_2$] (**6**), which dissolves only in Me$_2$SO, suggesting that bridge splitting and coordination of the solvent takes place. In fact, **6** reacts with 2-(methylthio)pyridine (1:1) in acetone to give the mononuclear insoluble complex [PdCl$_2$(SMepy)$_2$] (**7**) which can also be obtained by treatment of [PdCl$_2$(NCMe)$_2$] with the ligand in 1:2 molar ratio (see Scheme 2).

We have previously shown that acid-base reactions between Ag$_2$CO$_3$[7] or [Au(acac)PPh$_3$][3a] (acacH = acetylacetone) and protonated ligands, for example phosphonium salts, give ylide complexes. Similarly, reactions between Ag$_2$CO$_3$ or [Au(acac)PPh$_3$] with HSpy (2:1) or [SMepyH]ClO$_4$ (1:1) in acetone afford the insoluble complex [Ag$_2$(μ-Spy)$_2$] (**8**) or [Au(SMepy)PPh$_3$]ClO$_4$ (**9**), respectively (see Scheme 3).

Scheme 3



Schemes 2 and 3 show the proposed structures of complexes **1**–**9**. These are based on the well-established tendency of gold(I) to bond preferentially to sulfur rather than nitrogen, and the opposite preference for palladium(II). The similar tendency of silver(I) with respect to coordination by both types of ligands induces us to believe that in complexes **2** and **3** gold is bound to sulfur and silver to the nitrogen donor atom. Alternatively, the very insoluble complexes **2**, **3**, and **8** could also be formulated as polymers.

IR Spectra

The IR spectra of complexes **1**, **2**, and **4**–**9** show two strong bands in the 1600–1550 cm^{-1} region, which are assigned to ν_{CC} and ν_{CN} of the pyridine ring and correspond to those shown by their precursors SMepy (1613, 1576 cm^{-1}), [HSMepy]ClO$_4$ (1608, 1528 cm^{-1}), and [Au(Spy)$_2$]$^-$ (1586, 1570 cm^{-1}), respectively. The IR spectrum of **3** shows bands at 1262, 1132, 1094, and 1004 cm^{-1} corresponding to those shown by [Au(Sbz)$_2$]$^-$ at 1222, 1116, 1092, and 1000 cm^{-1}. The spectra of **1** and **2** lack the bands assignable to the PPN cation in the starting bis(thiolato)-gold(I) complexes [Au(Spy)$_2$]$^-$ and [Au(Sbz)$_2$]$^-$ [mainly at 1581, 1320–1220 (s, br), 544, 522 and 491 cm^{-1}] and those of the cationic complexes **1**, **4**, **5**, and **9** show two strong bands around 1100 (ν_{ClO}) and 620 (δ_{OClO}) assignable to the perchlorate anion. The palladium complexes **6** and **7** show ν_{PdCl} bands in the 300–350 cm^{-1} region, which in the case of **7** indicate a *trans* geometry. However, in complex **6** the similar *trans* influence of Cl-, N-, and S-donor ligands prevents any structural discussion.

NMR Spectra

The insolubility of complexes **2**, **3**, **5**, **7**, and **8** prevented measurement of their NMR spectra. As expected, the resonance due to SMe protons in the ^{1}H-NMR spectra of complexes **1** ([D$_6$]acetone), **4**, **5** (CD$_2$Cl$_2$), **6** ([D$_6$]DMSO), and **9** (CDCl$_3$) appears at lower field (δ = 2.6–4.0) than

the corresponding resonance for the free ligand SMepy (δ = 2.52). Complex **1** shows two resonances at δ = 2.97 and 3.83. Because of the presence of the two chiral sulfur centres they could be assigned to the *RR* + *SS* and *RS* isomers. The two separate Me resonances (in approx. 1:1 ratio) in the spectrum of **6** is indicative of the presence of the two possible geometrical isomers resulting from bridge splitting by [D_6]DMSO coordination. The resonances of the pyridyl protons appear as multiplets in the δ = 7–9 range. The spectrum of **6** shows four multiplets in this region. Three of them, in the δ = 7.2–7.8 region, correspond to protons 3- to 5-H of both isomers, whereas the proton in the 6 position gives a doublet for each isomer in the δ = 8.5–8.9 region. The presence of PPh_3 in complex **9** precludes the assignment of some of the resonances of the pyridine ring protons. In the ^{1}H-NMR spectrum of the free ligand SMepy the aromatic protons give complex multiplets centered at δ = 6.90 (1H, 4-H), 7.11 (1H, 3-H), 7.40 (1H, 5-H), and 8.4 (1H, 6-H), again at higher field than the corresponding resonances in the complexes. The spectrum of **4** shows also two broad singlets centered at δ = 2.51 and 3.50, which correspond to the protons of the tht ligand.

The $^{31}P\{^1H\}$-NMR spectra of **9** measured in $CDCl_3$ shows a resonance at δ = 29.6 (s).

The molar conductivity of the soluble complexes was measured on approx. $5 \cdot 10^{-4}$ M solutions in acetone, and the obtained values are in all cases in the range expected[8] for 1:1 (**4**, **5**, **9**) or 2:1 (**1**) electrolytes.

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Experimental

The IR spectra, elemental analyses, conductance measurements in acetone and melting-point determinations were carried out as described earlier[9]. – A Varian Unity-300 spectrometer was used to record ^{1}H- and $^{31}P\{^1H\}$-NMR spectra or a Bruker AC-200 for ^{1}H-NMR spectra. Chemical shifts are referred to TMS (^{1}H) or H_3PO_4 [$^{31}P\{^1H\}$]. – Reactions were carried out at room temperature without special precautions against moisture. The complexes of silver must be protected against daylight. **Warning:** Perchlorate salts with organic cations may be explosive.

HSpy was purchased from Fluka. 2-(methylthio)pyridine (SMepy) was obtained by the reaction of NaOH with (HSMepy)-ClO_4 (1:1 in acetone), and NMR data coincide with those reported[10]. (HSMepy)ClO_4 was prepared by treating $AgClO_4$ with (HSMepy)I (1:1 in acetone) which, in turn, was obtained by treating HSpy with MeI (1:6, net). The gold(I) complexes $[Au(Spy)_2]^-$ and $[Au(Sbz)_2]^-$ were prepared according to literature methods[4,11]. Ag_2CO_3 was prepared from $AgNO_3$ and Na_2CO_3 and $AgClO_4$ from Ag_2CO_3 and $HClO_{4(aq)}$.

[{Ag{μ-(SMepy)}}$_2$](ClO$_4$)$_2$ (**1**): To a solution of $AgClO_4$ (409.7 mg, 1.976 mmol) in acetone (15 ml) was added a solution of SMepy (247.4 mg, 1.976 mmol) in acetone (5 ml) over a period of 15 min, and the resulting solution was stirred for 30 min. It was then filtered through celite, concentrated (3 ml), and diethyl ether (20 ml) was added to precipitate **1** (388 mg) as a white solid which was filtered and air-dried. M.p. 205°C, yield 59%, Λ_M = 258 Ω^{-1} cm^2 mol^{-1} ($6.2 \cdot 10^{-4}$ M). – $C_{12}H_{14}Ag_2Cl_2N_2O_8S_2$ (665.0): calcd. C 21.67, H 2.12, N 4.21, S 9.64; found C 21.76, H 2.01, N 4.16, S 9.62. – IR (Nujol): $\tilde{\nu}$ = 1582, 1564, 1078, 618 cm^{-1}. – ^{1}H NMR ([D_6]acetone): δ = 2.97 (s, 3H, Me), 3.83 (s, 3H, Me), 7.54 (m, 2H, 4-H), 7.80 (d, $^3J_{HH}$ = 8 Hz, 2H, 3-H), 8.15 (m, 2H, 5-H), 8.69 (m, 2H, 6-H).

[AgAu{μ-(Spy)}$_2$] (**2**): Addition of solid $AgClO_4$ (44.6 mg, 0.206 mmol) to a suspension of PPN[Au(Spy)$_2$] (202.3 mg, 0.206 mmol) in acetone (5 ml) results in a yellow solution. A few minutes later a yellow suspension was formed which, after 30 min of stirring, was filtered off to give **2** (103 mg, 0.19 mmol) which was washed with dichloromethane (3 × 5 ml) and diethyl ether (5 ml) and air-dried. M.p. 115°C, yield 95%. – $C_{10}H_8AgAuN_2S_2$ (525.1): calcd. C 22.87, H 1.54, N 5.33, S 12.21; found C 22.43, H 1.37, N 4.96, S 11.97. – IR (Nujol): $\tilde{\nu}$ = 1576, 1552 cm^{-1}.

[AgAu{μ-(benzoxazol-2-yl)}$_2$] (**3**): Solid $AgClO_4$ (20.13 mg, 0.097 mmol) was added to a suspension of PPN[Au(benzoxazol-2-yl)$_2$] (100.6 mg, 0.097 mmol) and the resulting suspension stirred in the dark for 30 min. It was then centrifuged to separate **3** (52.3 mg, 0.086 mmol) as a white solid which was washed with dichloromethane (4 × 5 ml) and air-dried. M.p. 225°C, yield 89%. – $C_{14}H_8AgAuN_2O_2S_2$ (605.2): calcd. C 27.78, H 1.33, N 4.63, S 10.59; found C 27.86, H 1.25, N 4.51, S 9.97. – IR (Nujol): $\tilde{\nu}$ = 1262, 1132, 1094, and 1004 cm^{-1}.

[Au{SMepy}(tht)]ClO$_4$ (**4**): To a suspension of **1** (205 mg, 0.31 mmol) in dichloromethane (10 ml) was added [AuCl(tht)] (198.78 mg, 0.62 mmol), and the resulting suspension was stirred for 1 h. It was then filtered through celite to remove AgCl and some metallic gold. The solution was concentrated (2 ml) and diethyl ether (15 ml) added to precipitate **4** (149 mg, 0.29 mmol) as a white solid which was washed with diethyl ether (5 ml) and air-dried. M.p. 136°C, yield 47%, Λ_M = 134 Ω^{-1} cm^2 mol^{-1} ($4.5 \cdot 10^{-4}$ M). – $C_{10}H_{15}AuClNO_4S_2$ (509.8): calcd. C 23.56, H 2.96, N 2.75, S 12.58; found C 22.95, H 2.86, N 2.44, S 12.47. – IR (Nujol): $\tilde{\nu}$ = 1592, 1558, 1084, 622 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 2.21 (s, br, 4H, tht), 2.67 (s, 3H, SMe), 3.50 (s, br, 4H, tht), 7.38 ("t", 1H, 4-H), 7.45 ("d", 1H, 3-H), 7.97 ("t", 1H, 5-H), 8.45 ("d", 1H, 6-H).

[Au{SMepy}$_2$]ClO$_4$ (**5**): To a suspension of **4** (126.2 mg, 0.247 mmol) in dichloromethane (5 ml) was added SMepy (60 mg, 0.49 mmol), and the suspension was stirred for 30 min. It was then filtered through $MgSO_4$ to remove some metallic gold, the solution was concentrated (2 ml) and diethyl ether (20 ml) added to precipitate **5** (73 mg, 0.13 mmol) as a white solid which was washed with diethyl ether (5 ml) and air-dried. M.p. 170°C, yield 54%, Λ_M = 134 Ω^{-1} cm^2 mol^{-1} ($4.4 \cdot 10^{-4}$ M). – $C_{12}H_{14}AuClN_2O_4S_2$ (546.8): calcd. C 26.36, H 2.58, N 5.12, S 11.72; found C 26.49, H 2.67, N 4.84, S 12.24. – IR (Nujol): $\tilde{\nu}$ = 1592, 1558, 1084, 622 cm^{-1}. – ^{1}H NMR (CD_2Cl_2): δ = 2.70 (s, 3H, SMe), 7.42 (m, 4H, 3,4-H), 7.99 (m, 2H, 5-H), 8.53 (m, 2H, 6-H).

[{PdCl(μ-Cl){SMepy}}$_2$] (**6**): To a solution of [$PdCl_2$(NCPh$_2$)] (192.4 mg, 0.51 mmol) in acetone (15 ml) was added a solution of SMepy (62.8 mg, 0.51 mmol) in acetone (5 ml) dropwise. The orange suspension formed was stirred for 45 min and filtered off to give **6** (122 mg, 0.2 mmol) which was washed with diethyl ether (2 × 5 ml) and air-dried. M.p. 207°C (dec.), yield 80%. – $C_{12}H_{14}Cl_4N_2Pd_2S_2$ (605.0): calcd. C 23.82, H 2.33, N 4.63, S 10.60; found C 23.13, H 2.17, N 4.29, S 10.59. – IR (Nujol): $\tilde{\nu}$ = 1582, 1560, 343, 330, 302 cm^{-1}. – ^{1}H NMR ([D_6]DMSO): δ = 2.66 (s, 3H, SMe), 2.71 (s, 3H, SMe), 7.29 ("t", 2H, 4-H of both isomers), 7.47 (d, $^3J_{HH}$ = 8.3 Hz, 2H, 3-H of both isomers), 7.90 ("t", 2H, 5-H of both isomers), 8.53 (d, $^3J_{HH}$ = 5 Hz, 1H, 6-H of one isomer), 8.86 (d, $^3J_{HH}$ = 5.3 Hz, 1H, 6-H of the other isomer).

[{PdCl$_2${SMepy}}$_2$] (**7**): To a suspension of **6** (120.8 mg, 0.2 mmol) in acetone (10 ml) was added a solution of SMepy (60 mg,

0.4 mmol) in acetone (5 ml). The color of the resulting suspension slowly changed from orange to yellow. After 24 h of stirring it was filtered off, washed with diethyl ether (2 × 5 ml) and air-dried to give **7** (153 mg, 0.358 mmol). M.p. 220°C (dec.), yield 90%. – $C_{12}H_{14}Cl_2N_2PdS_2$ (427.7): calcd. C 33.70, H 3.30, N 6.55, S 14.99; found C 33.64, H 3.30, N 6.44, S 14.47. – IR (Nujol): $\tilde{\nu}$ = 1590, 1558, 349 cm^{-1}.

[Ag$_2${μ-(Spy)}$_2$] (**8**): To a suspension of Ag_2CO_3 (140.8 mg, 0.51 mmol) in acetone (8 ml) was added HSpy (113.52 mg, 1.02 mmol). The colour of the suspension changed into deep yellow. After it had been stirred for 30 min it was filtered off to give **8** (195 mg, 0.448 mmol) which was washed with diethyl ether (2 × 5 ml) and air-dried. M.p. 198°C (dec.), yield 88%. – $C_{10}H_8Ag_2N_2S_2$ (436.0): calcd. C 27.54, H 1.85, N 6.42; found C 27.16, H 1.60, N 6.12. – IR (Nujol): $\tilde{\nu}$ = 1580, 1570 cm^{-1}.

[Au{SMepy}PPh$_3$]ClO$_4$ (**9**): To a solution of (HSMepy)ClO_4 (64.65 mg, 0.29 mmol) in acetone (10 ml) was added solid [Au(acac)PPh_3] (160 mg, 0.29 mmol). The resulting solution was stirred for 30 min, filtered through celite, concentrated (3 ml) and diethyl ether (10 ml) added to precipitate an oily solid. It was washed with diethyl ether (2 × 10 ml), and stirred in *n*-pentane (15 ml) until **9** separated as a white solid which was filtered off and dried under nitrogen (163 mg, 0.24 mmol). M.p. 82°C, yield 82%. Λ_M = 141 Ω^{-1} cm^2 mol^{-1} ($5.9 \cdot 10^{-4}$ M). – $C_{24}H_{22}AuClNO_4PS$ (683.9): calcd. C 42.15, H 3.24, N 2.05, S 4.69; found C 41.62, H 3.14, N 2.06, S 4.67. – IR (Nujol): $\tilde{\nu}$ = 1590, 1558, 1088, 622 cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 2.73 (s, 3H, SMe), 7.51–7.68 (m, 17H, PPh_3 + 3,4-H), 8.04 ("t", 1H, 5-H), 8.62 (s, br, 1H, 6-H). – $^{31}P\{^1H\}$ NMR: δ = 29.6 (s).

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