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Compositional and Structural Variety of Diphenyllead(IV) Complexes Obtained by Reaction of Diphenyllead Dichloride with Thiosemicarbazones

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The reactions of $PbPh_2Cl_2$ in methanol with acetophenone, salicylaldehyde, pyridine-2-carbaldehyde, 2-acetylpyridine, and 2-benzoylpyridine thiosemicarbazones (HATSC, HSTSC, HPyTSC, HAcPyTSC, and HBPyTSC, respectively) were explored. Despite the similarities among these ligands, the reactions afforded solids with very diverse compositions and structural characteristics, which were in most cases analyzed by X-ray diffractometry (as was the structure of the free ligand HBPyTSC). In the complexes $[PbPh_2Cl_2(HATSC)]_2$, $[PbPh_2Cl_2(HSTSC)_2]$, $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$, and $[PbPh_2Cl(PyTSC)]$ the metal atoms are surrounded by more or less distorted octahedral coordination polyhedra; if both strong and weak interactions are considered, the lead atom in $[PbPh_2Cl(AcPyTSC)]$ has coordination number 7 and distorted pentagonal bipyramidal coordination geometry, while $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]\cdot 2MeOH$ contains two different types of lead atom, one with octahedral and the other with pentagonal bipyramidal coordination. The complexes $(H_2AcPyTSC)[PbPh_2Cl_3]$ and $[PbPh_2Cl(HAcPyTSC)][PbPh_2Cl_3]$, which were also isolated, could not be crystallized. All these complexes are soluble in DMSO, and the compositions of these solutions were investigated using conductivity measurements and ^1H and ^{207}Pb NMR spectroscopy.

1. Introduction

In recent years there has been a renaissance of interest in the coordination chemistry of lead[2,3] due in part to its intrinsic richness and also to the toxicological and environmental importance of this metal. Most of this recent work has been devoted to lead(II), possibly because it is assumed that this is the only oxidation state of relevance in biological systems. There is nevertheless clear evidence that intake of organolead compounds by mammals is only partly metabolized to and excreted as "inorganic" Pb(II).[4] Furthermore, there is no therapy for organolead poisoning, the chelating agents used to reduce the burden of other heavy metals not being effective against organolead.[4]

To add to the available information on the coordination behavior of organolead compounds we have begun to explore complexes derived from interaction between diphenyllead dichloride and thiosemicarbazone ligands (HTSCs, Chart 1). Although phenyllead derivatives are only used in organic synthesis[5] and have little environmental impact, they are relatively stable and will hopefully provide insight into R_n-Pb^{IV}−ligand interactions.

As far as we know, the reactions between $PbPh_2Cl_2$ and thiosemicarbazones have previously been investigated only by Dixit et al.,[6] who used IR and NMR spectroscopy to identify the complexes isolated. We show in this article that the solid-state structures of this type of complex, as determined by single-crystal X-ray crystallography, can be quite complicated, and we report ^1H and ^{207}Pb NMR data throwing light on their structures in DMSO solution.

2. Experimental Section

2.1. Materials. Acetophenone (Ega-Chemie), salicylaldehyde (Aldrich), pyridine-2-carbaldehyde (Aldrich), 2-acetylpyridine

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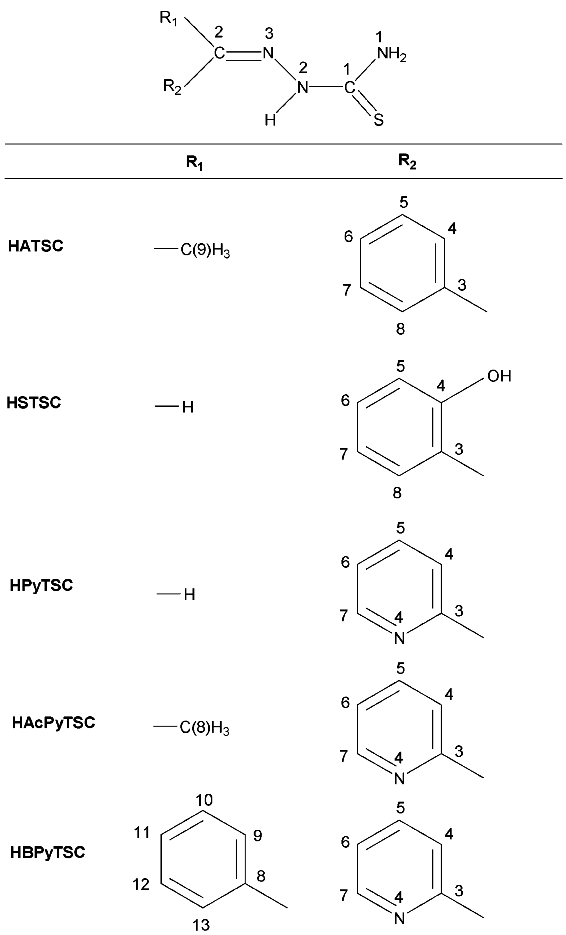
Table 1. Crystal and Refinement Data for HBPyTSC and the HTSC Complexes

	HBPyTSC	$[PbPh_2Cl_2(HATSC)]_2$	$[PbPh_2Cl_2(HSTSC)_2]$	$[\{PbPh_2Cl(HPyTSC)\}_2][(PbPh_2Cl_3(MeOH))]_2$	$[PbPh_2Cl(PyTSC)]$	$[PbPh_2Cl(AcPyTSC)]$	$[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]\cdot 2MeOH$
molecular formula	$C_{13}H_{12}N_4S$	$C_{42}H_{42}Cl_4N_6Pb_2S_2$	$C_{28}H_{28}Cl_2N_6O_2PbS_2$	$C_{64}H_{64}Cl_8N_8O_2Pb_4S_2$	$C_{19}H_{17}ClN_4PbS$	$C_{20}H_{19}ClN_4PbS$	$C_{64}H_{62}Cl_4N_8O_2Pb_3S_2$
M_r	256.33	1253.12	822.78	2153.76	576.07	590.09	1802.7
temp (K)	120(2)	293(2)	293(2)	293(2)	293(2)	293(2)	120(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
cryst system	monoclinic	triclinic	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.3340(2)	8.5712(2)	13.817(3)	9.907(2)	13.3359(3)	9.5816(17)	9.8300(5)
b (Å)	11.6570(2)	9.1760(2)	8.884(2)	12.604(3)	11.1170(3)	10.0802(18)	11.8780(6)
c (Å)	17.3750(4)	14.1713(3)	12.906(3)	15.834(4)	13.5689(2)	12.170(2)	14.8020(8)
α (deg)		90.6640(10)		109.016(4)		95.587(3)	77.330(2)
β (deg)	90.6540(10)	94.6720(10)	94.019(5)	92.413(4)	93.600(2)	104.252(3)	85.924(2)
γ (deg)		92.4770(10)		103.377(4)		114.979(2)	73.693(2)
V (Å^3)	2497.97(8)	1109.69(4)	1580.3(7)	1803.6(8)	2007.69(8)	1005.2(3)	1618.29(15)
Z	8	1	2	1	4	2	1
abs coeff (mm^{-1})	0.246	7.948	5.675	9.707	8.650	8.641	8.062
F(000)	1072	600	804	1016	1096	564	864
cryst size (mm)	0.20 × 0.20 × 0.28	0.06 × 0.10 × 0.10	0.23 × 0.17 × 0.06	0.26 × 0.12 × 0.25	0.1 × 0.06 × 0.02	0.19 × 0.26 × 0.37	0.10 × 0.15 × 0.60
θ range for data collcn (deg)	2.34−27.49	1.44−25.00	1.48−28.13	2.58−26.34	2.08−25.00	1.77−26.40	2.06−25.00
index ranges	0, 16; 0, 15; −22, 22	−10, 10; −10, 10; −16, 16	−18, 7; −1, 11; −17, 16	−12, 12; −15, 14; 0, 19	−15, 15; −13, 13; −16, 16	−11, 11; −12, 12; 0, 15	0, 11; −13, 14; −17, 17
reflcns collcd	5389	24 792	8318	7344	25 528	4087	10 405
goodness-of-fit on F^2	1.232	1.288	1.013	1.061	1.115	1.072	1.052
R1, wR2 [$I > 2\sigma(I)$]	0.0396, 0.1176	0.0245, 0.0731	0.0695, 0.1072	0.0252, 0.0528	0.0279, 0.0664	0.0164, 0.0398	0.0545, 0.1435
largest diff peak and hole (e Å^{-3})	0.376 and −0.540	0.660 and −1.985	2.317 and −1.607	1.044 and −0.948	1.319 and −1.511	0.628 and −1.113	2.14 and −2.41

Chart 1



(Aldrich), 2-benzoylpyridine (Aldrich), thiosemicarbazide (Merck), and dichlorodiphenyllead (Panreac), all of reagent grade, were used without further purification.

2.2. Physical Measurements. Elemental analyses for C, H, N, and S were performed with a Fisons 1108 microanalyzer. Melting points were determined with a Gallenkamp electrically heated apparatus. Conductance measurements were made using a Crison model microMC 2202 conductivity meter and samples prepared in anhydrous DMSO (Aldrich) under N_2 in a glovebox. NMR spectra were recorded in DMSO using a Bruker AMX 300 spectrometer at 300.14 MHz for ^1H spectra (with TMS as internal reference) and a Bruker AMX 500 at 104.58 MHz for ^{207}Pb spectra (using a saturated solution of $PbPh_4$ in $CDCl_3$, $\delta = -178.0$ ppm, as external reference). Elemental analysis and all spectroscopic measurements were carried out in the RIAIDT services of the University of Santiago de Compostela. X-ray data were collected at the RIAIDT services, at the CACTI services of the University of Vigo, and at the Sao Carlos Institute of Physics of the University of Sao Paulo.

2.3. X-ray Crystallography. Crystal data, experimental details, and refinement results are listed in Table 1. Data were collected on an Enraf-Nonius CAD-4 diffractometer (HBPyTSC, $[PbPh_2Cl_2(HATSC)]_2$, $[PbPh_2Cl(PyTSC)]$, and $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]\cdot 2MeOH$) or a Bruker Smart CCD1000 apparatus ($[PbPh_2Cl_2(HSTSC)_2]$, $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$, and $[PbPh_2Cl(AcPyTSC)]$). The structures were solved using direct methods (HBPyTSC, $[PbPh_2Cl_2(HATSC)]_2$, $[PbPh_2Cl(PyTSC)]$, $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)\cdot 2MeOH]$, and $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$) or the Patterson method ($[PbPh_2Cl_2(HSTSC)_2]$ and $[PbPh_2Cl(AcPyTSC)]$), followed by conventional difference Fourier techniques. All the H atoms were introduced in calculated positions except H(2A) and H(1S) in $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$, H(1N1) and H(2N1) in $[PbPh_2Cl(PyTSC)]$, and H(1A) and H(1B) in $[PbPh_2Cl(AcPyTSC)]$, which were located in the Fourier difference map and refined isotropically. The crystal of $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]\cdot 2MeOH$ presented disorder affecting the methanol molecules and the phenyl and pyridine rings of

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the thiosemicarbazone ligand, two atomic sites being observed for each of the atoms in these fragments. The site occupancy factors were determined as 0.600 and 0.400 for atoms in the pyridine rings, 0.700 and 0.300 for the phenyl rings, and 0.650 and 0.350 for the methanol molecules. Only the lengths of bonds between the atoms with the higher occupancy factors are included in the tables. The structure solution program used was SHELX 97.[7] Molecular graphics were obtained with ORTEP and PLATON.[8] Crystallographic data are available as Supporting Information and as deposited with the CCDC [CCDC Nos.: 198380 ($C_{13}H_{12}N_4S_1$); 198381 ($C_{42}H_{42}Cl_4N_6Pb_2S_2$); 198382 ($C_{28}H_{28}Cl_2N_6O_2PbS_2$); 198383 ($C_{64}H_{64}Cl_8N_8O_2Pb_4S_2$); 198384 ($C_{19}H_{17}ClN_4PbS$); 198385 ($C_{20}H_{19}ClN_4PbS$); 198386 ($C_{64}H_{62}Cl_4N_8O_2Pb_3S_2$].

2.4. Synthesis of the Ligands. HATSC, HSTSC, HPyTSC, HAcPyTSC, and HBPyTSC (Chart 1) were prepared by following the general procedure outlined by Anderson et al.[9] by reacting the thiosemicarbazide with the corresponding aldehyde or ketone in ethanol/water, as described in detail for HATSC elsewhere.[10] Only in the case of HATSC was it necessary for the synthesis to be carried out in the presence of glacial acetic.

2.4. Synthesis of the Complexes. The complexes were obtained by reacting $PbPh_2Cl_2$ and each thiosemicarbazone in methanol. In each case, 1:2, 1:1, and 2:1 mole ratios were used. Only syntheses in 1:2 mole ratio are described in detail.

Caution! *Lead is a highly toxic cumulative poison, and lead compounds should be handled carefully*.[4]

$PbPh_2Cl_2$/HATSC Reaction. To a solution of HATSC (0.09 g, 0.46 mmol) in MeOH (3 mL) was slowly added a suspension of $PbPh_2Cl_2$ (0.10 g, 0.23 mmol) in the same solvent (10 mL). The suspension dissolved partially, and after it was stirred for 24 h, a white solid formed which was filtered out and vacuum-dried. Yield: 89.3%. Mp: 200 °C. Anal. Calcd for $C_{21}H_{21}Cl_2N_3SPb$ ([$PbPh_2Cl_2$(HATSC)]$_2$): C, 40.3; H, 3.3; N, 6.7; S, 5.1. Found: C, 40.5; H, 3.9; N, 6.8; S, 5.8. Molar conductivity (10^{-3} M in DMSO): 4.4 Ω^{-1} cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6): δ[N(2)H] = 10.20 s (1); δ[N(1)H_2] = 8.26 s (1), 7.90 s (1); δ[C(4,8)H] = 7.92 m (2); δ[C(5−7)H] = 7.38 m (3); δ[H_o(Ph−Pb)] = 8.11 dd (4); δ[H_m(Ph−Pb)] = 7.59 t (4); δ[H_p(Ph−Pb)] = 7.42 t (2); ^3J(^{1}H−^{207}Pb) = 205.2 Hz; ^4J(^{1}H−^{207}Pb) = 82.2 Hz. ^{207}Pb NMR (DMSO-d_6): −507 ppm. Crystals suitable for X-ray diffraction analysis were obtained by crystallization from acetone/MeOH. Reactions in 2:1 and 1:1 mole ratios gave the same complex.

$PbPh_2Cl_2$/HSTSC Reaction. A suspension of $PbPh_2Cl_2$ (0.10 g, 0.23 mmol) in MeOH (7 mL) was added slowly with stirring to a solution of HSTSC (0.09 g, 0.46 mmol) in the same solvent (10 mL). The suspension was dissolved, and the yellow solution obtained was stirred for 48 h at room temperature. The white solid formed was filtered out and vacuum-dried. Yield: 58.2%. Mp: 217 °C. Anal. Calcd for $C_{28}H_{28}Cl_2N_6O_2S_2Pb$ ([$PbPh_2Cl_2$(HSTSC)$_2$]): C, 40.9; H, 3.4; N, 10.2; S, 7.8. Found: C, 41.2; H, 3.1; N, 10.3; S, 8.1. Molar conductivity (10^{-3} M in DMSO): 4.5 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6): δ[N(2)H] = 11.35 s (2); δ[N(1)H_2] = 8.08 s (2), 7.91 s (2); δ[OH] = 9.87 s (2); δ[C(2)H] = 8.36 s (2); δ[C(5)H] = 7.89 s (2); δ[C(6)H] = 7.20 td (2); δ[C(7,8)H] = 6.80 m (4); δ[H_o(Ph−Pb)] = 8.11 dd (4); δ[H_m(Ph−Pb)] = 7.59 t (4); δ[H_p(Ph−Pb)] = 7.44 t (2); ^3J(^{1}H−^{207}Pb) = 203.4 Hz; ^4J(^{1}H−^{207}Pb) = 82.2 Hz. ^{207}Pb NMR (DMSO-d_6): −506 ppm. Slow evaporation of the mother liquor at room temperature gave colorless crystals suitable for X-ray diffractometry. The same complex was afforded by 2:1 and 1:1 metal:ligand mole ratios.

$PbPh_2Cl_2$/HPyTSC Reaction. $PbPh_2Cl_2$ (0.10 g, 0.23 mmol) was suspended in 10 mL of MeOH and added slowly to a solution of HPyTSC (0.08 g, 0.46 mmol) in the same solvent (10 mL). $PbPh_2Cl_2$ rapidly dissolved, giving a clear yellow solution from which a new solid separated. The crystalline solid formed upon stirring this heterogeneous system overnight at room temperature was filtered out and dried under vacuum (yield: 0.12 g). It comprised two types of crystal, which were separated by hand under a microscope. One type is stable to air and moisture and proved to be [$PbPh_2Cl$(PyTSC)]. Mp: 204 °C. Anal. Calcd for $C_{19}H_{17}ClN_4PbS$: 39.6; H, 3.0; N, 10.0; S, 5.6. Found: C, 39.6; H, 2.9; N, 9.3; S, 5.4. Molar conductivity (10^{-3} M in DMSO): 18.5 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6, freshly prepared sample): δ[C(7)H] = 8.91 d (1); δ[C(2)H] = 8.53 s (1); δ[N(1)H_2] = 7.46 s (2); δ[C(4)H] = 7.63 d (1); the [C(5)H] and [C(6)H] signals overlap those of the phenyl groups; δ[H_o(Ph−Pb)] = 7.92 dd (4); δ[H_m(Ph−Pb)] = 7.44 t (4); δ[H_p(Ph−Pb)] = 7.31 t (2); ^3J(^{1}H−^{207}Pb) and ^4J(^{1}H−^{207}Pb) could not be calculated. The ^{1}H NMR spectrum of this compound rapidly becomes very complicated. ^{207}Pb NMR (DMSO-d_6 or DMF-d_6): no signal was observed.

Crystals of the other type became opaque with time and proved to be [{$PbPh_2Cl$(HPyTSC)}$_2$][$PbPh_2Cl_3$(MeOH)]$_2$. Mp: 227 °C. Anal. Calcd for $C_{32}H_{32}Cl_4N_4SOPb_2$: C, 35.7; H, 3.0; N, 5.2; S, 3.0. Found: C, 35.6; H, 2.7; N, 5.4; S, 2.7. Molar conductivity (10^{-3} M in DMSO): 6.5 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6): δ[N(2)H] = 11.62 s (2); δ[C(7)H] = 8.55 d (2); δ[N(1)H_2] = 8.33 s (2), 8.16 s (2); δ[C(4)H] = 8.26 d (2); δ[C(2)H] = 8.07 s (2); δ[C(5)H] = 7.83 t (2); δ[C(6)H] = 7.36 dd (2); δ[H_o(Ph−Pb)] = 8.15 d (16); δ[H_m(Ph−Pb)] = 7.60 t (16); δ[H_p(Ph−Pb)] = 7.43 t (8); ^3J(^{1}H−^{207}Pb) = 204.0 Hz; ^4J(^{1}H−^{207}Pb) = 82.7 Hz. ^{207}Pb NMR (DMSO-d_6): −506 ppm.

The reaction in 1:1 mole ratio also afforded a mixture of both complexes, while reaction in 2:1 mole ratio gave only [{$PbPh_2Cl$(HPyTSC)}$_2$][$PbPh_2Cl_3$(MeOH)]$_2$. Both complexes were studied by X-ray diffractometry.

$PbPh_2Cl_2$/HAcPyTSC Reaction. A suspension of $PbPh_2Cl_2$ (0.10 g, 0.23 mmol) in MeOH (10 mL) was added with stirring to a yellow suspension of HAcPyTSC (0.09 g, 0.46 mmol) in the same solvent (10 mL). The orange solution obtained was stirred for 4 h at room temperature. The yellow solid formed, probably $PbPh_2Cl_2$(HAcPyTSC)(HCl) or (H_2AcPyTSC)[$PbPh_2Cl_3$] (see Discussion), was filtered out and dried in vacuo. Yield: 53%. Mp: 207 °C. Anal. Calcd for $C_{20}H_{21}Cl_3N_4SPb$: C, 36.2; H, 3.2; N, 8.5; S, 4.8. Found: C, 37.0; H, 3.3; N, 8.9; S, 5.1. Molar conductivity (10^{-3} M in DMSO): 8.2 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6): δ[N(2)H] = 10.50 s (1); δ[C(7)H] = 8.64 d (1); δ[N(1)H_2] = 8.51 s (1), 8.33 s (1); δ[C(4)H] = 8.40 d (1); δ[C(5)H] = 7.00 t (1); δ[C(6)H] overlaps signals of the phenyl groups; δ[C(8)H_3] = 2.38 s (3); δ[H_o(Ph−Pb)] = 8.15 d (4); δ[H_m(Ph−Pb)] = 7.47 t (4); δ[H_p(Ph−Pb)] = 7.40 t (2); ^3J(^{1}H−^{207}Pb) = 206 Hz; ^4J(^{1}H−^{207}Pb) = 82.3 Hz. The fact that water signal is very wide seems likely to be due to the presence of an unresolved pyridinium proton signal (the same phenomenon has been also observed in the proton spectrum of 2-acetylpyridine thiosemicarbazone hydrochloride,

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which is known to contain the $[H_2AcPyTSC]^+$ ion in the solid state[11]). ^{207}Pb NMR (DMSO-d_6): −507 ppm.

Partial evaporation of the mother liquor afforded a small amount of a mixture containing small plates of the free ligand and orange crystals suitable for X-ray study that turned out to be $[PbPh_2Cl(AcPyTSC)]$. Mp: 195 °C. Anal. Calcd for $C_{20}H_{19}ClN_4SPb$: C, 40.7; H, 3.2; N, 9.5; S, 5.4. Found: C, 40.4; H, 3.3; N, 9.3; S, 5.3. Molar conductivity (10^{-3} M in DMSO): 23.8 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6): δ[C(7)H] = 8.96 d (1); δ[C(5)H] = 7.97 t (1); δ[C(4)H] = 7.86 (overlapping H$_o$); δ[C(6)H] = 7.45 m (1); δ[N(1)-H$_2$] = 7.43 s (2); δ[C(8)H$_3$] = 2.54 s (3); δ[H$_o$(Ph−Pb)] = 7.86 dd (4); δ[H$_m$(Ph−Pb)] = 7.41 t (4); δ[H$_p$(Ph−Pb)] = 7.28 t (2); $^3J(^1H-^{207}Pb)$ = 196.5 Hz. $^4J(^1H-^{207}Pb)$ could not be calculated. ^{207}Pb NMR (DMSO-d_6): −493 ppm.

When $PbPh_2Cl_2$ and HAcPyTSC were mixed in 1:1 and 2:1 mole ratios in the same solvent and stirred overnight, a pale yellow solid formed which was filtered out and dried in vacuo. Yield: 41%. Mp: 208 °C. Anal. Calcd for $C_{32}H_{30}Cl_4N_4Pb_2S$ ($[PbPh_2Cl(HAcPyTSC)][PbPh_2Cl_3]$): C, 36.3; H, 2.8; N, 5.3; S, 3.0. Found: C, 36.4; H, 2.9; N, 5.3; S, 3.0. Molar conductivity (10^{-3} M in DMSO): 7.5 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6): δ[N(2)H] = 10.30 s (1); δ[C(7)H] = 8.56 d (1); δ[C(6)H] = 8.42 d (1); δ[N(1)-H$_2$] = 7.39 s (1), 8.11 s (1, overlapping H$_o$); δ[C(5)H] = 7.77 m (1); δ[C(6)H] = 7.37 m (1); δ[C(8)H$_3$] = 2.54 s (3); δ[H$_o$(Ph−Pb)] = 8.11 dd (8); δ[H$_m$(Ph−Pb)] = 7.60 t (8); δ[H$_p$(Ph−Pb)] = 7.42 t (4); $^3J(^1H-^{207}Pb)$ = 204.3 Hz; $^4J(^1H-^{207}Pb)$ = 82.0 Hz. ^{207}Pb NMR (DMSO-d_6): −507 ppm.

$PbPh_2Cl_2$/HBPyTSC Reaction. To a solution of HBPyTSC (0.15 g, 0.58 mmol) in MeOH (7 mL), a suspension of $PbPh_2Cl_2$ (0.13 g, 0.30 mmol) in the same solvent (9 mL) was slowly added with stirring. The yellow solution obtained was stirred for 4 h at room temperature, affording after slow evaporation a yellow solid, $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]\cdot 2MeOH$. Yield: 43.4%. Mp: 194 °C. Anal. Calcd for $C_{64}H_{62}Cl_4N_8O_2S_2Pb_3$: C, 42.6; H, 3.5; N, 6.2; S, 3.6. Found: C, 42.8; H, 3.3; N, 6.4; S, 3.7. Molar conductivity (10^{-3} M in DMSO): 5.8 S cm^2 mol^{-1}. ^{1}H NMR (DMSO-d_6; see Figure 10): δ[C(7)H] = 8.96 d (2); δ[C(5)H] = 7.71 td (2); δ[N(1)-H$_2$] = 7.30 s (4); δ[C(9−13)H] = 7.10−7.50 (overlapping Ph−Pb); δ[C(4)H] = 6.80 d (2); δ[C(6)H] overlaps signals of the phenyl groups; δ[H$_o$(Ph−Pb)] = 8.16 d (4), 7.98 d (8); δ[H$_m$(Ph−Pb)] = 7.57 t (4), 7.45 t (8); δ[H$_p$(Ph−Pb)] = 7.2−7.5 m; $^3J(^1H-^{207}Pb)$ = 206.1, 195.5 Hz. ^{207}Pb NMR (DMSO-d_6): −504.2 ppm. Crystallization of this yellow solid from a 1:1 EtOH−CH_2Cl_2 solution yielded crystals of the complex suitable for X-ray diffraction analysis. The same complex was isolated by reacting $PbPh_2Cl_2$ and the ligand in 2:1 and 1:1 mole ratios.

The mother liquor subsequently gave crystals of HBPyTSC which were used in the X-ray study of the free ligand (vide infra). ^{1}H NMR (DMSO-d_6): δ[N(2)H] = 12.52 s (1); δ[C(7)H] = 8.87 d (1); δ[N(1)H$_2$] = 8.66 s (1), 8.21 s (1); δ[C(5)H] = 8.02 t (1); δ[C(9,13)H] = 7.66 d (2); δ[C(6)H] = 7.61 m (1); δ[C(10−12)H] = 7.46 d (3); δ[C(4)H] = 7.38 d (1).

3. Results and Discussion

3.1. Synthesis of the Complexes. All reactions were performed by mixing a suspension of $PbPh_2Cl_2$ in methanol with a solution of the corresponding HTSC in the same solvent until a 1:2, 1:1, or 2:1 mole ratio was reached. In 1:2 mole ratio, in all cases except one the halide dissolved, giving a clear solution from which one or more complexes were eventually isolated. Mixtures in 1:1 and 2:1 mole ratios were generally suspensions.

Although one might expect that the selected thiosemicarbazones should all give similar compounds, the results were amazingly dissimilar.

HATSC and HSTSC were not deprotonated under any of the mole ratio conditions used, giving only 1:1 HATSC or 1:2 HSTSC adducts.

The reactions of $PbPh_2Cl_2$ with HPyTSC in 1:2 and 1:1 mole ratios both gave two complexes simultaneously. In one, the deprotonated ligand has displaced one of the two chlorides from the coordination sphere of the metal, giving the neutral mixed complex $[PbPh_2Cl(PyTSC)]$. In the other the chloride ion is also displaced, but HPyTSC retains its proton, forming the cationic complex $[\{PbPh_2Cl(HPyTSC)\}_2]^{2+}$. Only this latter was formed when the mole ratio was 2:1.

Reaction of $PbPh_2Cl_2$ with HAcPyTSC in 1:2 mole ratio afforded the $[PbPh_2Cl(PyTSC)]$ analogue $[PbPh_2Cl(AcPyTSC)]$, but (probably due to its greater solubility) it was isolated only after isolation of a product that seems to be $[H_2AcPyTSC][PbPh_2Cl_3]$. The latter seems likely to have originated from interaction of the excess ligand with the HCl generated when $[PbPh_2Cl(AcPyTSC)]$ formed. Its elemental analysis agrees with the proposed formula (see Experimental Section), and its ^{1}H NMR spectrum in DMSO is coherent with the presence of the $H_2AcPyTSC^+$ cation. Furthermore, metal complexes containing the counterion $[H_2AcPyTSC]^+$ have been reported previously.[12,13] Since the protonation constants of HAcPyTSc and HPyTSC are almost identical,[14,15] it is plausible that a similar complex containing $[H_2PyTSC]^+$ may have been formed in the reaction of $PbPh_2Cl_2$ with HPyTSC, in which case its nonisolation might be due to it being more instead of less soluble than $[PbPh_2Cl(PyTSC)]$ ($[H_2PyTSC]Cl$ is more soluble than $[H_2AcPyTSC]Cl$ in MeOH according to our approximate measurements).

When reacted in 1:1 and 2:1 mole ratio, $PbPh_2Cl_2$ and HAcPyTSC afforded a compound that was tentatively formulated as $[PbPh_2Cl(HAcPyTSC)][PbPh_2Cl_3]$ by analogy with that obtained using $PbPh_2Cl_2$ and HPyTSC (vide supra)(bar the MeOH ligand).

Finally, the reaction of HBPyTSC with $PbPh_2Cl_2$ afforded the same product regardless of mole ratio: in all cases the deprotonated ligand displaced the two chlorides from $PbPh_2Cl_2$, giving the positively charged fragment $[PbPh_2(BPyTSC)]^+$. Two of these fragments interact weakly with a $PbPh_2Cl_4^{2-}$ moiety (vide infra), giving the final complex $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]$, which was isolated solvated with two molecules of methanol.

The above results suggest that all these reactions involve complex equilibria including the displacement of chloride ligand(s) from the coordination sphere of the lead by the

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Table 2. Selected Bond Lengths (Å) and Angles (deg) in $[PbPh_2Cl_2(HATSC)]$, $[PbPh_2Cl_2(HSTSC)_2]$, $[PbPh_2(PyTSC)Cl]$, and $[PbPh_2(AcPyTSC)Cl]$

	$[PbPh_2Cl_2(HATSC)]_2$[a]	$[PbPh_2Cl_2(HSTSC)_2]$[b]	$[PbPh_2Cl(PyTSC)]$	$[PbPh_2Cl(AcPyTSC)]$[b]
Pb−C(11)	2.185(5)	2.185(10)	2.181(5)	2.191(3)
Pb−C(21)	2.203(5)		2.192(5)	2.186(3)
Pb−Cl(1)	2.8352(11)	2.715(3)	2.7425(12)	2.7949(9)
Pb−Cl(2)	2.6511(12)			
Pb−Cl(1)^i	2.8549(11)			
Pb−S	2.7832(12)	2.819(2)	2.5825(13)	2.7345(9)
Pb−S^i				3.0851(9)
Pb−N(3)			2.494(4)	2.585(2)
Pb−N(4)			2.759(4)	2.486(2)
C(11)−Pb−C(21)	177.18(13)		149.33(19)	176.16(11)
C(11)−Pb−C(11)^i		180.0		
C(11)−Pb−Cl(2)	89.66(13)			
C(21)−Pb−Cl(2)	90.66(13)			
C(11)−Pb−N(3)			98.67(16)	87.91(10)
C(21)−Pb−N(3)			92.97(14)	95.07(11)
C(11)−Pb−S	91.02(12)	91.9(3)	105.67(14)	96.68(9)
C(21)−Pb−S	86.16(12)		104.88(13)	86.71(8)
N(3)−Pb−S			72.31(9)	67.37(6)
Cl(2)−Pb−S	98.14(4)			
N(3)−Pb−Cl(1)			156.17(9)	152.39(6)
C(11)−Pb−Cl(1)	89.89(12)	90.3(3)	88.77(13)	89.25(9)
C(21)−Pb−Cl(1)	92.89(12)		91.90(12)	86.98(9)
Cl(2)−Pb−Cl(1)	93.15(4)			
S−Pb−Cl(1)	168.68(4)	92.19(9)	83.89(5)	140.21(2)
C(11)−Pb−Cl(1)^i	88.15(12)	98.7(3)		
C(21)−Pb−Cl(1)^i	91.94(13)			
Cl(2)−Pb−Cl(1)^i	171.18(4)			
S−Pb−Cl(1)^i	90.45(4)			
Cl(1)−Pb−Cl(1)^i	78.31(3)	180.0		
C(21)−Pb−S^i				93.18(9)
C(11)−Pb−S^i		88.1(3)		86.89(9)
N(3)−Pb−S^i				124.47(6)
N(4)−Pb−S^i				167.21(6)
S−Pb−S^i		179.999(1)		61.45(3)
Cl(1)−Pb−S^i		87.81(9)		79.75(3)
C(11)−Pb−N(4)			73.64(15)	90.47(10)
C(21)−Pb−N(4)			86.91(16)	88.62(11)
N(3)−Pb−N(4)			62.89(12)	64.86(8)
S−Pb−N(4)			134.23(9)	131.33(6)
Cl(1)−Pb−N(4)			140.73(9)	84.71(6)

[a] Symmetry operations: $i = -x, -y, -z$. [b] Symmetry operations: $i = 1 - x, 1 - y, 1 - z$.

HTSC ligand (and probably also by the solvent) and the deprotonation equilibrium of the thiosemicarbazone. This conclusion is supported by the ^1H NMR spectrum of a 1:1 mixture of $PbPh_2Cl_2$ and HAcPyTSC in CD_3OH, which shows a complex pattern of broad bands (the 1:2 mixture is rather insoluble and quickly produces a precipitate in the NMR tube). It seems probable that the identity of the solid complex isolated is determined by the relative solubilities of the various species in each system together with the small differences in donor capacity and pK_a among the HTSCs.

3.2. Solid-State Structures. Figure 1 shows the molecular structure and numbering of the adduct $[PbPh_2Cl_2(HATSC)]_2$. Selected bond lengths and angles are listed in Table 2. The compound is a centrosymmetric dimer in which each metal atom is coordinated to one carbon of each of two phenyl groups, to one thiosemicarbazone sulfur, to one terminal chloride [Cl(2)], and to two bridging chlorides [Cl(1) and Cl(1)^i, $i = -x, -y, -z$]. The lead atom is thus octahedrally coordinated, the main distortion of this geometry affecting the bond angles Cl(1)−Pb-Cl(1)^i [78.31(3)°] and S−Pb−Cl(1) [168.68(4)°]. The Pb−C and bridging Pb−Cl distances are longer than in the polymeric compound $PbPh_2Cl_2$,[16] probably because of the strong bond with the terminal Cl. As might be expected, the Pb−S bond is significantly longer than in complexes containing the deprotonated thiosemicar-

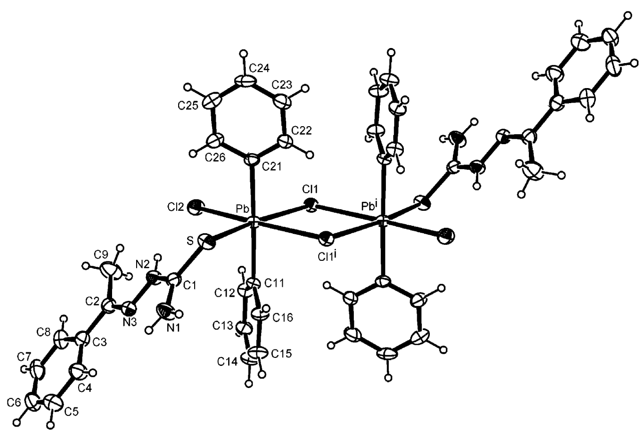

Figure 1. Molecular structure of $[PbPh_2Cl_2(HATSC)]_2$.

bazone ligand (vide infra). About the C(1)−N(2) and C(2)−N(3) bonds HATSC has the EE configuration that is usually found in free thiosemicarbazones. It is practically planar [SC(1)N(1)N(2)N(3)C(2) to C(9), rms = 0.0337] and forms a dihedral angle of 67.56(0.04)° with the plane containing Pb, S, Cl(1), Cl(2), and Cl(1)^i (rms = 0.826). The C(1)−S distance, though longer than in free thiosemicarbazone ligands,[17] indicates the persistence of significant double bond character, being close to that previously found in $[NiCl_2(HATSC)]$.[18] The other bond lengths in the thiosemicarbazone chain are within the ranges of values previously found in neutral thiosemicarbazones.

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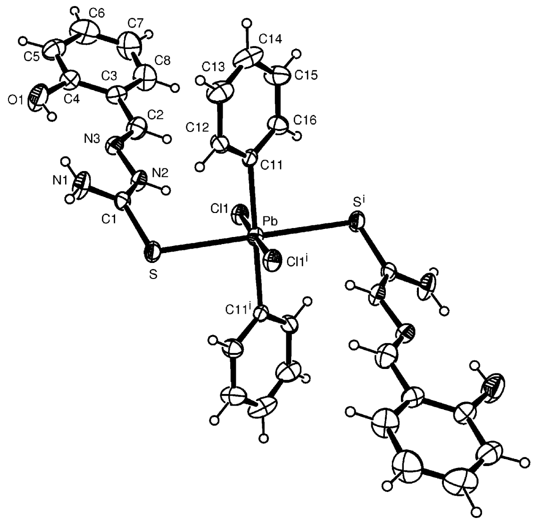

Figure 2. Molecular structure of $[PbPh_2Cl_2(HSTSC)_2]$.

The Cl atoms, N(3), and the $N(1)H_2$ and N(2)H groups are all involved in intra- or intermolecular hydrogen bonds (see Table 5), the latter of which give rise to a polymeric chain along the *x* axis as shown in Figure 1S (here and hereafter, the suffix "S" indicates figures included in the Supporting Information).

$[PbPh_2Cl_2(HSTSC)_2]$ (Figure 2) is a centrosymmetric monomer in which the lead atom is coordinated to two phenyl groups, two chloride anions, and two thiosemicarbazone sulfur atoms in an octahedral arrangement with a slight degree of distortion [the bond angles around the metal range from 87.81(9) for $Cl-Pb-S^i$ ($i = 1 - x, 1 - y, 1 - z$) to 92.19(9)° for S−Pb−Cl (see Table 2)]. The Pb−C bonds are the same length as in $[PbPh_2Cl_2(HATSC)]_2$, while the Pb−Cl distance is between the two displayed by the latter adduct. However, the Pb−S distance is slightly longer in the 1:2 adduct.

The coordination behavior of HSTSC in this adduct (neutral and monodentate) is not common for this ligand, which is usually bideprotonated and S,N(3),O-tridentate. It has only been found previously in the X-ray diffraction study of the Cu(I) adduct $[Cu(PPh_3)_2Br(HSTSC)]$.[19] As in that case, HSTSC is almost planar and retains the EE conformation found in the free ligand,[20] a small elongation of the C−S bond being the only significant structural change in the ligand upon coordination.

Three intramolecular hydrogen bonds help stabilize the molecules, and one intermolecular hydrogen bond links them in a two-dimensional network in the *y*−*z* plane (see Table 5 and Figure 2S).

The asymmetric unit of $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$ is shown together with its numbering scheme in Figure 3, and selected bond lengths and angles are listed in Table 3. Unlike the adducts previously described, there are two independent units in this compound: one, containing Pb(1), is a cation in which the central metal of diphenyllead(IV) is also coordinated to a chloride and to an undeprotonated thiosemicarbazone ligand, while the other, containing Pb(2), is an anion in which the diphenyllead(IV) center coordinates to three chlorides and the oxygen of a methanol molecule. The cationic units are linked in pairs by chloro

Table 3. Selected Bond Lengths (Å) and Angles (deg) in $[PbPh_2Cl(HPyTSC)][PbPh_2Cl_3(MeOH)]$[a]

Pb(1)−C(21)	2.178(5)	S−C(1)	1.682(5)
Pb(1)−C(11)	2.181(5)	C(1)−N(1)	1.318(6)
Pb(1)−N(3)	2.606(4)	C(1)−N(2)	1.349(6)
Pb(1)−N(4)	2.686(4)	C(2)−N(3)	1.260(6)
Pb(1)−S	2.7890(14)	C(2)−C(3)	1.455(7)
Pb(1)−Cl(1)	2.7898(14)	C(3)−N(4)	1.354(6)
Pb(1)−Cl(1)^i	2.9112(13)	C(3)−C(4)	1.367(7)
Pb(2)−C(41)	2.167(5)	C(4)−C(5)	1.382(8)
Pb(2)−C(31)	2.168(5)	C(5)−C(6)	1.362(9)
Pb(2)−O(1S)	2.554(5)	C(6)−C(7)	1.377(8)
Pb(2)−Cl(4)	2.6318(14)	C(7)−N(4)	1.336(7)
Pb(2)−Cl(3)	2.6671(14)	N(2)−N(3)	1.374(6)
Pb(2)−Cl(2)	2.8147(15)	O(1S)−C(1S)	1.421(9)
C(21)−Pb(1)−C(11)	172.59(18)	C(41)−Pb(2)−Cl(4)	95.53(14)
C(21)−Pb(1)−N(3)	92.88(15)	C(31)−Pb(2)−Cl(4)	90.96(13)
C(11)−Pb(1)−N(3)	82.53(15)	O(1S)−Pb(2)−Cl(4)	87.97(14)
C(21)−Pb(1)−N(4)	86.25(16)	C(41)−Pb(2)−Cl(3)	94.90(14)
C(11)−Pb(1)−N(4)	86.44(16)	C(31)−Pb(2)−Cl(3)	96.93(13)
N(3)−Pb(1)−N(4)	61.66(12)	O(1S)−Pb(2)−Cl(3)	176.87(13)
C(21)−Pb(1)−S	89.04(13)	Cl(4)−Pb(2)−Cl(3)	89.97(4)
C(11)−Pb(1)−S	94.66(14)	C(41)−Pb(2)−Cl(2)	87.57(14)
N(3)−Pb(1)−S	68.62(10)	C(31)−Pb(2)−Cl(2)	87.45(13)
N(4)−Pb(1)−S	129.68(9)	O(1S)−Pb(2)−Cl(2)	99.22(14)
C(21)−Pb(1)−Cl(1)	95.03(13)	Cl(4)−Pb(2)−Cl(2)	172.48(5)
C(11)−Pb(1)−Cl(1)	92.12(12)	Cl(3)−Pb(2)−Cl(2)	82.93(4)
N(3)−Pb(1)−Cl(1)	143.05(9)	N(3)−C(2)−C(3)	120.8(5)
N(4)−Pb(1)−Cl(1)	154.84(9)	N(4)−C(3)−C(4)	122.7(5)
S−Pb(1)−Cl(1)	75.47(4)	N(4)−C(3)−C(2)	116.7(5)
C(21)−Pb(1)−Cl(1)^i	92.23(12)	C(4)−C(3)−C(2)	120.6(5)
C(11)−Pb(1)−Cl(1)^i	87.74(13)	C(3)−C(4)−C(5)	119.6(6)
N(3)−Pb(1)−Cl(1)^i	140.88(10)	C(6)−C(5)−C(4)	118.3(6)
N(4)−Pb(1)−Cl(1)^i	80.04(9)	C(5)−C(6)−C(7)	119.3(6)
S−Pb(1)−Cl(1)^i	150.24(4)	N(4)−C(7)−C(6)	123.6(6)
Cl(1)−Pb(1)−Cl(1)^i	74.80(4)	C(1)−N(2)−N(3)	121.7(4)
C(41)−Pb(2)−C(31)	166.50(19)	C(2)−N(3)−N(2)	117.3(4)
C(41)−Pb(2)−O(1S)	82.96(18)	C(7)−N(4)−C(3)	116.5(5)
C(31)−Pb(2)−O(1S)	85.47(17)		

[a] Symmetry operations: $i = -x + 1, -y + 2, -z$.

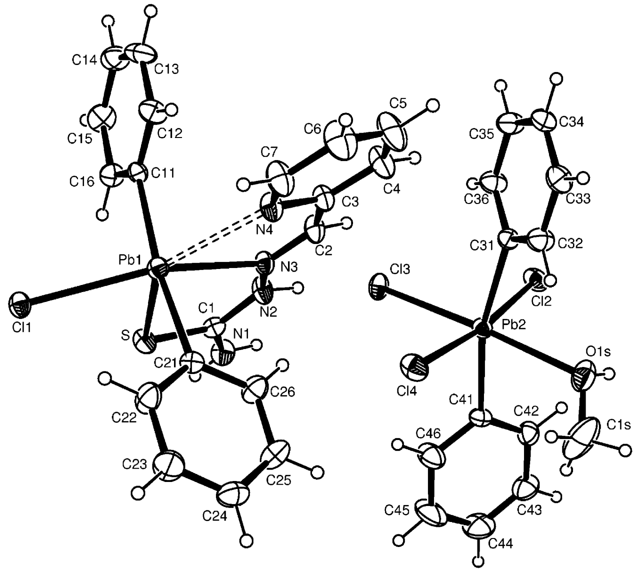

Figure 3. Molecular structure of $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$ showing one of the $\{PbPh_2Cl(HPyTSC)\}^+$ moieties and the $[PbPh_2Cl_3(MeOH)]^-$ anion.

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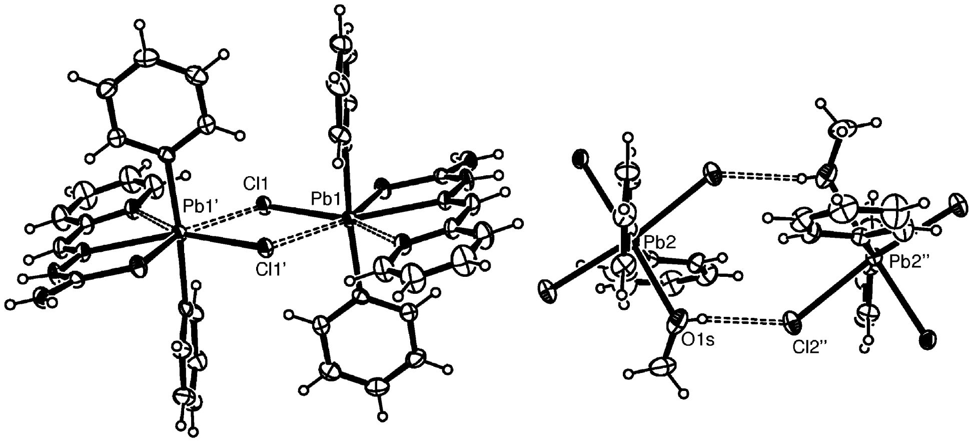

Figure 4. View of $[\{PbPh_2Cl(HPyTSC)\}_2][PbPh_2Cl_3(MeOH)]_2$ showing the doubly charged dinuclear cation $[\{PbPh_2Cl(HPyTSC)\}_2]^{2+}$ and the weak association of the $[PbPh_2Cl_3(MeOH)]^-$ anions in pairs.

bridges [Pb(1)$\cdots$Cl(1)^i = 2.9112(13) Å; i = $-x + 1, -y + 2, -z$], giving rise to the doubly charged dinuclear cation $[\{PbPh_2Cl(HPyTSC)\}_2]^{2+}$ (Figure 4). The formation of this dimer gives a coordination number of 7 to Pb(1), which has a distorted pentagonal bipyramidal coordination polyhedron with both phenyl groups axial. The HPyTSC ligand, though undeprotonated, suffers the usual conformational change from EE to ZZ to allow S,N(3),N(4)-tridentate coordination, and its plane (rms = 0.0714) makes an angle of 11.44(0.12)° with the equatorial plane of the complex [Pb(1)SN(3)N(4)-Cl(1)Cl(1)^i, rms = 0.1071]. Its placing three donor atoms in the coordination sphere of the lead atom displaces one of the $PbPh_2Cl_2$ chlorides, which then probably coordinates to another $PbPh_2Cl_2$ molecule to form a $[PbPh_2Cl_3]^-$ anion that evolves to $[PbPh_2Cl_3(MeOH)]^-$ by coordination to the oxygen atom of a solvent molecule. This gives Pb(2) octahedral coordination with Cl(2), Cl(3), Cl(4), and O(1S) equatorial (rms = 0.0484). The main distortion of the octahedral symmetry affects the angle C(31)$-$Pb(2)$-$C(41), which deviates about 14° from linearity. Two Cl$\cdots$H$-$O hydrogen bonds weakly link the anions in pairs (Figure 4), and other hydrogen bonds involving $N(1)H_2$, N(2)H, O(1S)H, Cl(2), and Cl(3) groups (see Table 5) connect the dimeric cations with pairs of anions, giving rise to a two-dimensional network (Figure 4S).

The molecular structure of $[PbPh_2Cl(PyTSC)]$ is shown together with the numbering scheme in Figure 5, and selected bond lengths and angles are listed in Table 2. In this complex the Ph_2Pb^{IV} moiety is coordinated to a Cl and to the S, N(3), and N(4) atoms of a pyridine-2-carbaldehyde thiosemicarbazonato ligand. The geometry of the coordination sphere around the metal can be described as a distorted pentagonal bipyramid with one vacant equatorial position, the phenyl groups being axial and the lead atom about 0.11 Å from the equatorial plane defined by S, N(3), N(4), and Cl (rms = 0.0947). The main distortion from the ideal geometry is probably imposed by the strong coordination of the metal to the S and N(3) atoms and by the small bite of the ligand, all of which bends C$-$Pb$-$C toward the vacant space in the equatorial plane, narrowing this angle by ca. 30° from linearity. There are no other interactions involving the metal. Deprotonation and coordination to the metal cause the usual changes in the thiosemicarbazone ligand,[17] namely a switch from *E* to *Z* conformation with respect to C(1)$-$N(2) and significant evolution of the C(1)$-$S bond from the thione to the thiol form. In keeping with the latter change, the Pb$-$S bond in this complex is significantly shorter than in the two adducts with undeprotonated ligands described above (see Table 3). The plane of the pyridine ring (rms = 0.008) makes a dihedral angle of 13.35(0.26)° with that of the chain SC-(1)C(2)N(1)N(2)N(3) (rms = 0.0317). Two intermolecular hydrogen bonds involving the $N(1)H_2$ group and N(2) and Cl atoms link the molecules in zigzag layers (see Table 5 and Figure 5S).

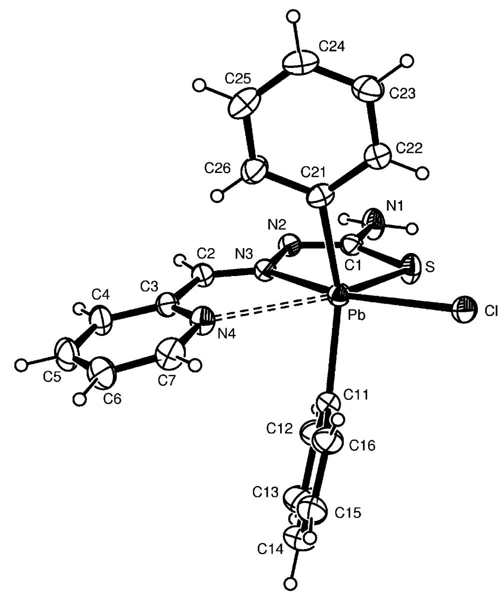

Figure 5. Molecular structure of $[PbPh_2Cl(PyTSC)]$.

The asymmetric unit of $[PbPh_2Cl(AcPyTSC)]$ is shown together with the numbering scheme in Figure 6, and selected bond lengths and angles are listed in Table 2. Despite the similarity of HPyTSC and HAcPyTSC, their interactions in the solid state with $[PbPh_2Cl]^+$ differ somewhat. As in $[PbPh_2Cl(PyTSC)]$, the thiosemicarbazonate ligand in $[PbPh_2Cl(AcPyTSC)]$ coordinates to the metal through its S, N(3), and N(4) atoms, but the shortest metal$-$ligand bond is in

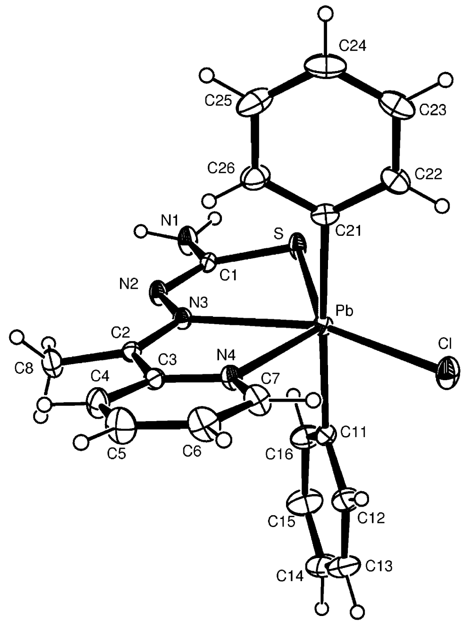

Figure 6. Molecular structure of [$PbPh_2Cl$(AcPyTSC)] showing the monomer.

this case Pb−N(4), while Pb−S and Pb−N(3) are longer than in the $PyTSC^-$ complex. This weakening of Pb−S allows a weak S⋯Pb^i interaction with the metal atom of a neighboring molecule to link the complexes in pairs (Figure 7; i = 1 − *x*, 1 − *y*, 1 − *z*). Thus [$PbPh_2Cl$(AcPyTSC)], unlike [$PbPh_2Cl$(PyTSC)], has all the positions of its pentagonal bipyramidal coordination sphere occupied, and the C−Pb−C angle deviates only ca. 4° from linearity. By contrast, the equatorial plane $PbSS^iN(3)N(4)Cl$ is rather distorted (rms = 0.1388), mainly due to the S and N(3) atoms. The chelate rings SC(1)N(2)N(3)Pb (rms = 0.078) and PbC(2)C(3)N(3)N(4) (rms = 0.0469) form a dihedral angle of 7.54(0.08)°, and neither is exactly coplanar with the pyridine ring. Upon deprotonation and coordination to the metal the free ligand[21] undergoes changes similar to those of $PyTSC^-$ in [$PbPh_2Cl$(PyTSC)], although the longer Pb−S bond in the $AcPyTSC^-$ complex entails a slightly shorter C(1)−S bond indicative of less evolution toward the thiol form (see Table 2). As in [$PbPh_2Cl$(PyTSC)], there are two intermolecular hydrogen bonds involving the $N(1)H_2$ group, Cl, and N(2) (see Table 5 and Figure 7), although in this case one of these bonds stabilizes the dimer originated by the Pb⋯S^i interaction and the second links the dimers in one-dimensional chains.

Figure 8 shows the molecular structure and numbering scheme of HBPyTSC. Bond lengths and bond angles are listed in Table 4. The S−C(1), N(1)−C(1), N(2)−C(1), N(2)−N(3), and N(3)−C(2) bond lengths are similar to the mean values found among the free HTSC structures in the CSD.[17,22] Comparison of these parameters with typical lengths of single and double bonds[23] shows that in the thiosemicarbazone moiety of HBPyTSC there is extensive electron delocalization.

As in other thiosemicarbazones, an intramolecular hydrogen bond involving $N(1)H_2$ and N(3) [N(1)⋯N(3) = 2.576(2), N(1)−H(1A) = 0.880, H(1A)⋯N(3) = 2.202 Å; N(1)−H(1A)⋯N(3) = 105.1°] stabilizes the *E* configuration with respect to the C(1)−N(2) bond (Figure 8), while another intramolecular hydrogen bond involving N(2)H and N(4) [N(2)⋯N(4) = 2.635(19), N(2)−H(2A) = 0.880, H(2A)⋯N(4) = 1.979 Å; N(2)−H(2A)⋯N(4) = 130.4°] doubtless helps stabilize the *Z* configuration about the C(2)−N(3) bond (*E* configuration is found in most unsubstituted pyridine-derived thiosemicarbazones,[21,24−28] and this intramolecular bond has been observed only once before on unsubstituted ligand of this type[29]). Besides these intramolecular hydrogen bonds, there is an intermolecular hydrogen bond between the sulfur atom and the $N(1)H_2$ group which links the molecules in pairs (see Figure 8, N(1)−H(1B)⋯S^i [i = −*x*, −1 − *y*, −*z*;

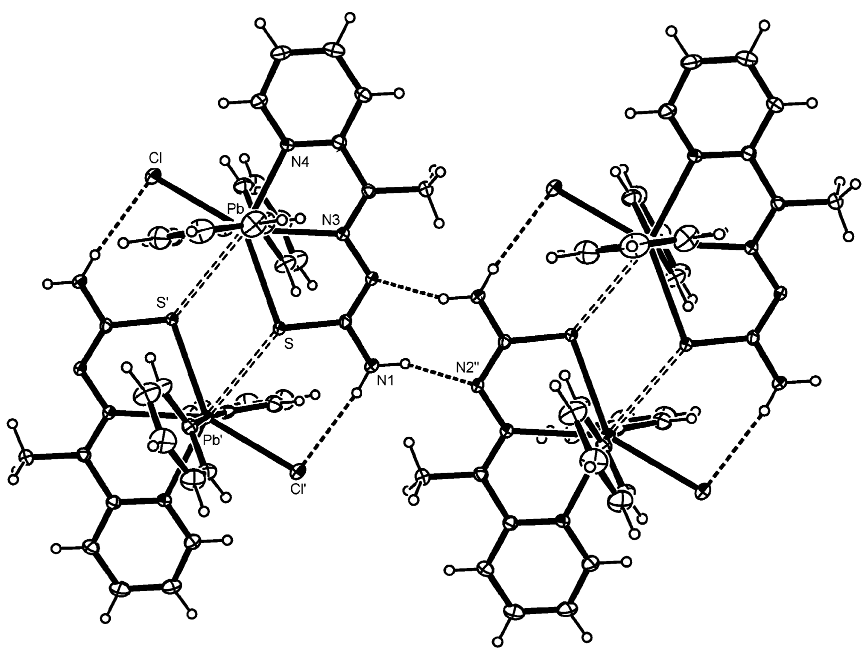

Figure 7. Molecular structure of [$PbPh_2Cl$(AcPyTSC)] showing the weak S⋯Pb^i interaction (i = 1 − *x*, 1 − *y*, 1 − *z*) and some hydrogen bonds that reinforce and link the dimers.

Table 4. Selected Bond Lengths (Å) and Angles (deg) in HBPyTSC and [{$PbPh_2(BPyTSC)$}$_2$($PbPh_2Cl_4$)]·2MeOH[a]

	HBPyTSC		
S−C(1)	1.6790(16)	N(3)−C(2)	1.297(2)
N(1)−C(1)	1.330(2)	C(2)−C(3)	1.488(2)
N(2)−C(1)	1.367(2)	N(4)−C(7)	1.337(2)
N(2)−N(3)	1.3684(18)	N(4)−C(3)	1.355(2)
C(1)−N(2)−N(3)	117.12(13)	N(1)−C(1)−S	124.71(13)
C(2)−N(3)−N(2)	121.09(13)	N(3)−C(2)−C(8)	112.44(13)
N(2)−C(1)−N(1)	115.92(14)	N(3)−C(2)−C(3)	127.36(14)
N(2)−C(1)−S	119.37(12)		
	[{$PbPh_2(BPyTSC)$}$_2$($PbPh_2Cl_4$)]·2MeOH		
Pb(1)−C(31)	2.190(12)	Pb(2)−Cl(1)	2.751(3)
Pb(1)−C(21)	2.196(13)	S−C(1)	1.703(13)
Pb(1)−N(3)	2.457(9)	N(1)−C(1)	1.362(15)
Pb(1)−S	2.577(3)	N(2)−C(1)	1.337(15)
Pb(1)−N(4)	2.585(10)	N(2)−N(3)	1.361(13)
Pb(1)−Cl(1)	2.974(3)	N(3)−C(2)	1.307(14)
Pb(1)−Cl(2)	3.448(3)	C(2)−C(3)	1.535(15)
Pb(2)−C(41)	2.196(11)	N(4)−C(7)	1.3900
Pb(2)−Cl(2)	2.727(3)	N(4)−C(3)	1.3900
C(31)−Pb(1)−C(21)	159.2(5)	Cl(1)−Pb(1)−Cl(2)	70.46(7)
C(31)−Pb(1)−N(3)	91.1(4)	C(41)^i−Pb(2)−C(41)	180.0
C(21)−Pb(1)−N(3)	98.8(4)	C(41)^i−Pb(2)−Cl(2)	90.2(3)
C(31)−Pb(1)−S	101.8(3)	C(41)−Pb(2)−Cl(2)	89.8(3)
C(21)−Pb(1)−S	98.5(3)	Cl(2)−Pb(2)−Cl(2)^i	180.0
N(3)−Pb(1)−S	73.6(2)	C(41)−Pb(2)−Cl(1)	91.5(3)
C(31)−Pb(1)−N(4)	82.3(5)	Cl(2)−Pb(2)−Cl(1)	85.66(8)
C(21)−Pb(1)−N(4)	85.0(5)	C(41)−Pb(2)−Cl(1)^i	88.5(3)
N(3)−Pb(1)−N(4)	66.4(4)	Cl(2)−Pb(2)−Cl(1)^i	94.34(8)
S−Pb(1)−N(4)	139.9(4)	Cl(1)−Pb(2)−Cl(1)^i	180.0
C(31)−Pb(1)−Cl(1)	85.0(3)	Pb(2)−Cl(1)−Pb(1)	107.44(9)
C(21)−Pb(1)−Cl(1)	96.4(4)	C(1)−S−Pb(1)	99.7(4)
N(3)−Pb(1)−Cl(1)	146.0(2)	C(1)−N(2)−N(3)	115.2(10)
S−Pb(1)−Cl(1)	74.21(9)	C(2)−N(3)−N(2)	115.9(10)
N(4)−Pb(1)−Cl(1)	145.5(4)	N(2)−C(1)−N(1)	113.6(11)
C(31)−Pb(1)−Cl(2)	88.2(3)	N(2)−C(1)−S	130.2(9)
C(21)−Pb(1)−Cl(2)	77.9(3)	N(1)−C(1)−S	116.3(9)
N(3)−Pb(1)−Cl(2)	143.3(2)	N(3)−C(2)−C(8)	126.6(15)
S−Pb(1)−Cl(2)	142.2(9)	N(3)−C(2)−C(3)	115.9(11)
N(4)−Pb(1)−Cl(2)	77.2(4)		

[a] Symmetry operations: i = $-x + 2$, $-y + 1$, $-z$.

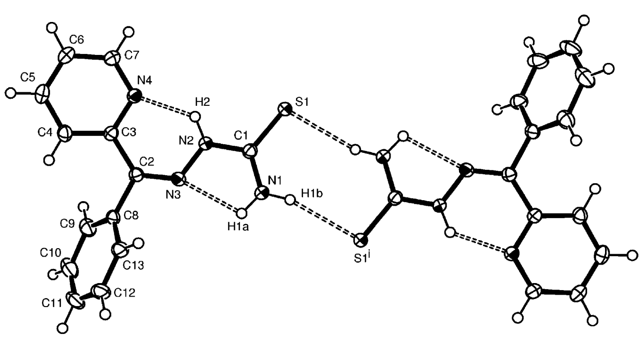

Figure 8. Molecular structure of HBPyTSC showing the intra- and intermolecular hydrogen bonds.

N(1)···S^i = 3.341(15), N(1)−H(1B) = 0.88, H(1B)···S^i = 2.492 Å; N(1)−H(1B)···S^i = 162.5°].

Figure 9 shows the molecular structure and numbering scheme of [{$PbPh_2(BPyTSC)$}$_2$($PbPh_2Cl_4$)]·2MeOH. Bond lengths and bond angles are listed in Table 4 together with those of HBPyTSC. The complex is trinuclear and centrosymmetric, containing two {$PbPh_2(BPyTSC)$} units linked by a {$PbPh_2Cl_4$} unit. In the latter the Pb(2) atom is octahedrically coordinated to two phenyl groups and four chloride ions, the Pb−C distance [2.196(11) Å] being shorter and the Pb−Cl distances [Pb(2)−Cl(2) = 2.728(3), Pb(2)−Cl(1) = 2.751(3) Å] slightly longer than the sums of the corresponding covalent radii (2.37 and 2.59 Å, respectively[23]). The environment of the lead atom is similar in $PbPh_2Cl_2$,[16] but in the {$PbPh_2Cl_4$} unit the Pb−C bonds are slightly shorter, while Pb(2)−Cl(2) is shorter and Pb(2)−Cl(1) longer than the Pb−Cl bonds in $PbPh_2Cl_2$.[16] The chlorine atoms also coordinate, albeit weakly, to the two Pb(1)-based units [Pb(1)···Cl(1) = 2.974(3), Pb(1)···Cl(2) = 3.447(3) Å]. The Cl^- ligand that is the more strongly bound to Pb(2), Cl(2), is the more weakly bound to Pb(1), the Pb(1)−Cl(2) bond length being close to the sum of the van der Waals radii of the atoms (3.70 Å[23]). Together with the two chlorides, a carbon atom of each of the two phenyl groups and the sulfur atom and two nitrogen atoms of the thiosemicarbazonate ligand make the coordination number of Pb(1) up to 7, giving a coordination sphere that is best

Table 5. Intra- and Intermolecular Hydrogen Bonds in the Complexes (Å, deg)

	D−H	H···A	D···A	D−H···A
[$PbPh_2Cl_2(HATSC)$]$_2$[a]				
N(1)−H(1A)···N(3)	0.860	2.250	2.606(7)	140.4
N(2)−H(2)···Cl(2)	0.860	2.763	3.576(4)	158.4
N(1)−H(1B)···Cl(1)^{ii}	0.860	3.020	3.373(5)	107.0
N(1)−H(1A)···Cl(2)^{ii}	0.860	2.818	3.532(5)	141.4
[$PbPh_2Cl_2(HSTSC)_2$][b]				
O(1)−H(1)···N(3)	0.820	2.002	2.710(12)	145.9
N(1)−H(1A)···N(3)	0.860	2.384	2.702(14)	102.3
N(1)−H(1B)···Cl(1)^{ii}	0.860	2.489	3.314(11)	160.9
N(2)−H(1A)···Cl(1)	0.860	2.374	3.233(9)	178.0
[{$PbPh_2Cl(HPyTSC)$}$_2$][$PbPh_2Cl_3(MeOH)$]$_2$[c]				
N(2)−H(2A)··Cl(3)	0.87(5)	2.28(5)	3.144(4)	173(4)
O(1S)−H(1S)··Cl(2)^{ii}	0.66(6)	2.46(6)	3.107(5)	166(7)
N(1)−H(1B)··Cl(2)^{iii}	0.86	2.45	3.292(5)	168.1
N(1)−H(1A)··Cl(3)^{iii}	0.86	2.83	3.311(4)	117.3
[$PbPh_2(PyTSC)Cl$][d]				
N(1)−H(1N1)···N(2)^i	0.889(19)	2.26(2)	3.135(6)	168(5)
N(1)−H(2N1)···Cl^{ii}	0.88(2)	2.49(3)	3.306(5)	154(5)
[$PbPh_2(AcPyTSC)Cl$][e]				
N(1)−H(1A)···Cl^i	0.81(4)	2.57(4)	3.367(3)	167(4)
N(1)−H(1B)···N(2)^{ii}	0.92(5)	2.28(5)	3.149(4)	157(4)
[{$PbPh_2(BPyTSC)$}$_2$($PbPh_2Cl_4$)]·2MeOH[f]				
N(1)−H(1A)···O(1S)^{ii}	0.880	1.974	2.8268(16)	162.80
N(1)−H(1B)···Cl(1)^{iii}	0.880	2.661	3.426(11)	145.97

[a−f] Symmetry operations: (*a*) ii = $1 + x$, y, z; (*b*) ii = $1 - x$, $0.5 + y$, $0.5 - z$; (*c*) ii = $2 - x$, $1 - y$, $1 - z$, iii = $2 - x$, $2 - y$, $1 - z$; (*d*) i = $-x$, $1 - y$, $1 - z$, (ii) = $-0.5 - x$, $-0.5 + y$, $0.5 - z$; (*e*) i = $1 - x$, $1 - y$, $1 - z$, (ii) $2 - x$, $2 - y$, $1 - z$; (*f*) ii = x, $1 + y$, z, (iii) = $1 - x$, $2 - y$, $-z$.

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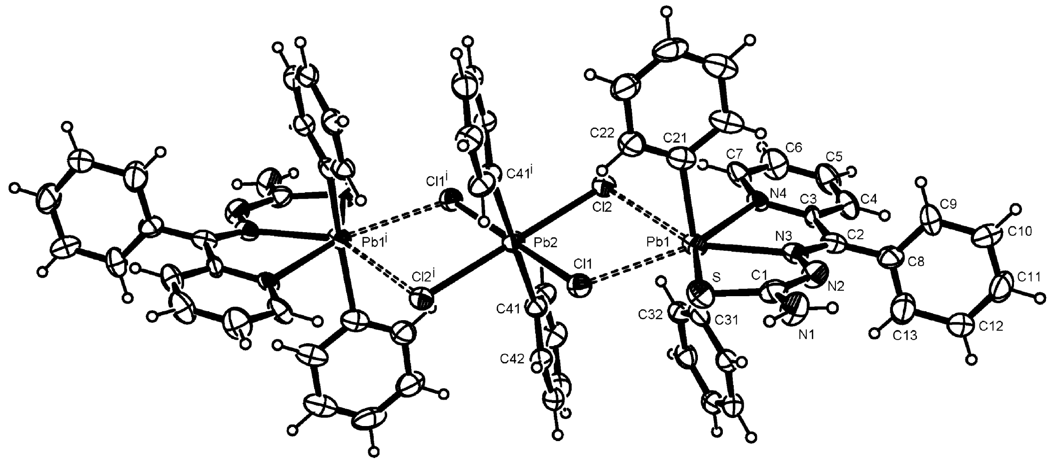

Figure 9. Molecular structure of $[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)]\cdot 2MeOH$.

described as a distorted pentagonal bipyramid. Unfortunately, the disorder shown by the pyridine and phenyl rings of the $BPyTSC^-$ ligand prevents thorough analysis of all the changes undergone by HBPyTSC (vide supra) upon the formation of the complex. However, in the thiosemicarbazone chain deprotonation and coordination to the metal basically bring about the same changes as in the thiosemicarbazonate ligand in $[PbPh_2Cl(PyTSC)]$: a switch to *Z* conformation about the C(1)−N(2) bond, a lengthening of the C(1)−S and C(1)−N(1) bonds, and a shortening of C(1)−N(2). The Pb−S and Pb−N(3) bonds are slightly shorter in the $BPyTSC^-$ complex than in $[PbPh_2Cl(PyTSC)]$ and significantly shorter than in $[PbPh_2Cl(AcPyTSC)]$, while Pb−N(4) is longer than in the latter complex but shorter than in the former. An intermolecular hydrogen bond between N(1)−H(1B) and a Cl(1) (see Table 5) links the molecules in a polymeric chain (see Figure 9S), while the solvent molecules are bound by hydrogen bonds involving N(1)−H(1A) [or $N(1)^i-H(1A)^i$] and their oxygen atom (Table 5, Figure 9S).

3.3. Studies in DMSO Solution. The new compounds are all insoluble in $CHCl_3$ but soluble in DMSO. The molar conductivity of 10^{-3} M solutions is <10 S cm^2 mol^{-1} in all cases except those of $[PbPh_2Cl(PyTSC)]$ and $[PbPh_2Cl(AcPyTSC)]$, which have values of 18.5 and 23.8 S cm^2 mol^{-1}, respectively, that are still far less than those expected for 1:1 electrolytes in this solvent (50−70 S cm^2 mol^{-1} [30]) and hence rule out extensive ionogenous dissociation.

The high receptivity and abundance of ^{207}Pb facilitate NMR spectroscopy.[31] The spectrum of a 2×10^{-2} M solution of $PbPh_2Cl_2$ in DMSO shows a single signal at −508.4 ppm which may be due to the previously described adduct $[PbPh_2Cl_2(DMSO)_2]$.[32] The ^{207}Pb NMR data for the HTSC complexes containing neutral thiosemicarbazone ligands suggest that they all dissociate in DMSO in accordance with the equation

$$[PbPh_2Cl_2(HTSC)_n] + 2DMSO \rightarrow [PbPh_2Cl_2(DMSO)_2] + n\text{HTSC}$$

their signals all lying close to that of $PbPh_2Cl_2$. The ^{1}H NMR data are also coherent with this conclusion, the chemical shifts and coupling constants corresponding in all cases with those of $PbPh_2Cl_2$ and the free HTSC ligands in DMSO.

$[PbPh_2Cl(PyTSC)]$ turned out to be unstable in DMSO solution, decomposing within a few minutes and so allowing only the ^{1}H NMR spectrum to be recorded (see Experimental Section). This spectrum shows changes relative to the free ligand and diphenyllead chloride which are in keeping with the deprotonation and coordination of HPyTSC: (i) The N(2)−H signal at 11.65 ppm in the spectrum of HPyTSC disappears. (ii) The two signals associated with $N(1)H_2$ in the free ligand, at 8.37 and 8.10 ppm, merge into one because in the complex this group can rotate freely as a consequence of the change in the charge distribution in the thioamide group when the S−Pb bond forms. (iii) The C(2)−H signal (at 8.07 ppm in the free ligand) shifts downfield due to the coordination of N(3) to the metal. (iv) The C(7)−H signal (at 8.53 ppm in the free ligand) also shifts downfield, due to the inductive effect of the Pb−N(4) bond. (v) All the protons of the phenyl groups are more shielded than in $PbPh_2Cl_2$.

For $[PbPh_2Cl(AcPyTSC)]$, both ^{1}H and ^{207}Pb NMR spectra in DMSO were obtained. In the proton spectrum, the changes in the ligand signals upon deprotonation and coordination are basically the same as those described above for $[PbPh_2Cl(PyTSC)]$, suggesting similar coordination via S, N(3), and N(4). Surprisingly, the ^{207}Pb NMR signal is located at only slightly lower field than that of $PbPh_2Cl_2$, at −493 as against −508.4 ppm. Since the kernels of these compounds are different, this similarity is probably due to their lead atoms also having different coordination numbers: 6 in $PbPh_2Cl_2$(solv) and 7 in $[PbPh_2Cl(AcPyTSC)]$, in which even if the dimer-forming $Pb\cdots S^i$ bonds (vide supra) are broken in solution they are probably replaced by bonds to DMSO molecules.

^{1}H and ^{207}Pb NMR spectra were also recorded for the complex formed by the deprotonated HBPyTSC ligand,

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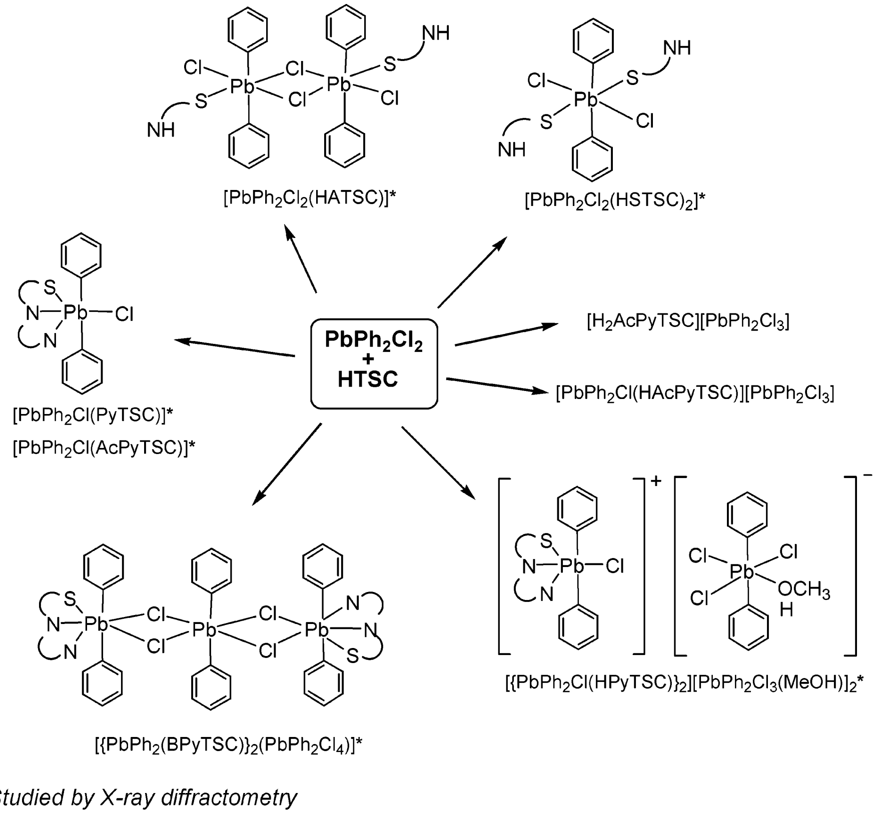
Scheme 1



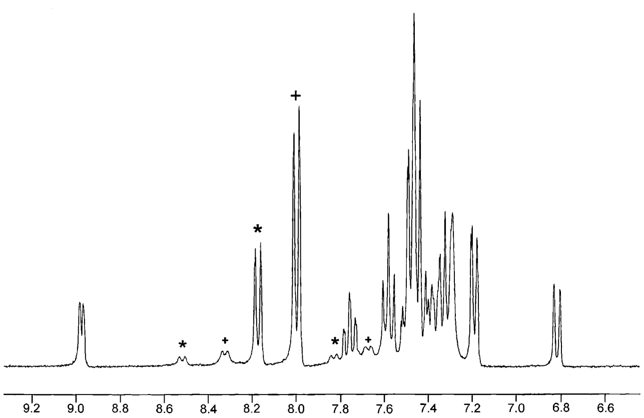


Figure 10. ^{1}H NMR spectrum of [{$PbPh_2$(BPyTSC)}$_2$($PbPh_2Cl_4$)]·2MeOH from 6.6 to 9.2 ppm. An asterisk indicates a signal corresponding to H_o(Pb−Ph) in $PbPh_2Cl_2$, and a plus sign indicates a signal corresponding to H_o(Pb−Ph) in [$PbPh_2$Cl(BPyTSC)].

[{$PbPh_2$(BPyTSC)}$_2$($PbPh_2Cl_4$)]·2MeOH. In the ^{1}H spectrum (Figure 10), the changes in the ligand signals with respect to those of the free ligand are similar to those observed in the spectra of [$PbPh_2$Cl(PyTSC)] and [$PbPh_2$Cl(AcPyTSC)], suggesting deprotonation and a similar coordination mode (as was also observed crystallographically). Among the organometallic signals, however, the presence and intensities of two clearly different signals for the *ortho* protons, with their corresponding coupling constants, indicate the existence of two different kernels in 2:1 ratio. The chemical shift and coupling constant of the less intense signal, 8.16 ppm and 206.1 Hz, coincide with data for $PbPh_2Cl_2$ in DMSO, suggesting the formation of this species, while the chemical shift and coupling constant of the more intense signal, 7.98 ppm and 195.5 Hz, agree well with values obtained for these protons in the complexes in which the $[PbPh_2]^{2+}$ unit coordinates to both thiosemicarbazonate and chloride anions. These data suggest that the following process must take place in DMSO solution:

$$[\{PbPh_2(BPyTSC)\}_2(PbPh_2Cl_4)] \xrightarrow{DMSO} [PbPh_2Cl_2(DMSO)_2] + 2[PbPh_2Cl(BPyTSC)]$$

The position of the only signal in the ^{207}Pb NMR spectrum of this complex in DMSO shows that it corresponds to [$PbPh_2Cl_2$(DMSO)$_2$]. No signal for [$PbPh_2$Cl(BPyTSC)] was obtained even though the solution seems to be stable (the ^{1}H NMR spectrum remained unaltered for several days). The Pb−N_{Py} bond being weaker than in [$PbPh_2$Cl(AcPyTSC)], it seems possible that the solvent displaces the N(4) atom from the coordination sphere and thereby allows the conformation of the ligand with respect to the C(2)−N(3) bond to vary, thus providing a relaxation mechanism for the ^{207}Pb nucleus via the influence of the π charge of the phenyl and pyridinyl groups.

3.4. Conclusions. The reaction of $PbPh_2Cl_2$ with thiosemicarbazones in methanol proceeds without observable dephenylation, giving a variety of diphenyllead(IV) complexes with diverse compositions and configurations in the solid state (see Scheme 1). Only the HTSCs which include a pyridine ring as an additional donor center are able to displace the chloride ligand from the coordination sphere of the metal. This displacement can be accompanied by deprotonation of the HTSC, giving thiosemicarbazonates. The other HTSCs investigated only form adducts.

In keeping with its size, in all these compounds the lead atom has coordination number 6 or 7, often using Cl^- as a bridging ligand in order to increase the number of available donor atoms. The C−Pb−C angle of the $PbPh_2$ unit can narrow to only 150° but usually remains close to the 180° of $PbPh_2Cl_2$.

The solvent MeOH seems to compete poorly with the chloride and thiosemicarbazone ligands, because only once was it included in the coordination sphere of lead in the solid state.

The complexes containing undeprotonated HTSC ligands dissociate in DMSO, giving the starting materials. Those containing thiosemicarbazonate ligands either persist or evolve to new complexes, but the ligand remains coordinated to the metal atom.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[PbPh_2Cl_2(HATSC)]_2$, $[PbPh_2Cl_2(HSTSC)_2]$, $[PbPh_2Cl(PyTSC)]$, $[PbPh_2Cl(AcPyTSC)]$, $[\{PbPh_2Cl(HPyTSC)\}_2]$-$[PbPh_2Cl_3(MeOH)]_2$, HBPyTSC, and $[\{PbPh_2(BPyTSC)\}_2(PbPh_2$-$Cl_4)]\cdot 2MeOH$, Figure 1S (polymeric chains along the *x* axis in the $[PbPh_2Cl_2(HATSC)]_2$ lattice formed by intermolecular hydrogen bonds), Figure 2S (intra- and intermolecular hydrogen bonds in $[PbPh_2Cl_2(HSTSC)_2]$), Figure 4S (hydrogen bonds connecting the dimeric cations with pairs of anions in $[\{PbPh_2Cl(HPyTSC)\}_2]$-$[PbPh_2Cl_3(MeOH)]_2$), Figure 5S (intermolecular hydrogen bonds in $[PbPh_2Cl(PyTSC)]$), and Figure 9S (the intermolecular hydrogen bond between N(1)−H(1b) and Cl(1) which links $[\{PbPh_2$-$(BPyTSC)\}_2(PbPh_2Cl_4)]$ molecules in polymeric chains and also the hydrogen bonds with the MeOH solvent molecules). This material is available free of charge via the Internet at http://pubs.acs.org.

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