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Interaction of organolead(IV) derivatives with formyl- and acetylferrocene thiosemicarbazones: Coordination versus dephenylation or reductive elimination processes

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Abstract

The reaction of Ph_2PbCl_2 with formylferrocene and acetylferrocene thiosemicarbazones (HTSCs) in methanol afforded the corresponding adduct $[Ph_2PbCl_2(HTSC)_2]$ or, in one case, the complex $[Ph_2PbCl(TSC)]$. X-ray crystallography of four of the adducts showed them to be all-*trans* octahedral complexes with the HTSC ligand S-bound to the metal. The IR spectrum of $[Ph_2PbCl(TSC)]$ suggests that the TSC^- ligand is N,S-coordinated. The reaction of $Ph_2Pb(OAc)_2$ with HTSCs in methanol gave either $[Ph_2Pb(OAc)_2(HTSC)_2]$ or $[Ph_2Pb(OAc)(TSC)]$, which was also obtained from $Ph_3Pb(OAc)$ via a spontaneous dephenylation process. In the former complexes the HTSC ligand is S-coordinated in the solid state. X-ray crystallography of two of the four $[Ph_2Pb(OAc)(TSC)]$ complexes showed that the thiosemicarbazonate anion is N,S-coordinated and the acetate is anisobidentate. Cyclic voltammetry of one $[Ph_2PbCl_2(HTSC)_2]$ adduct and the corresponding $[Ph_2Pb(OAc)(TSC)]$ complex showed that the inductive effect of coordination to lead is transmitted to the ferrocenyl group. Surprisingly, the reaction of $Me_2Pb(OAc)_2$ with HTSCs afforded only $[Pb(TSC)_2]$ complexes, possibly via redistribution and reductive elimination processes.

Keywords: Diphenyllead(IV) complexes; Triphenyllead(IV); Dephenylation; Dimethyllead(IV); Reductive elimination; Formylferrocene thiosemicarbazones; Acetylferrocene thiosemicarbazones; X-ray structures; Mass spectra; IR spectra; ^1H, ^{13}C and ^{207}Pb NMR spectra; Cyclic voltammetry

1. Introduction

Pb–C bonds are rather weak, reported energies ranging from 134 to 142 kJ mol^{-1} (*cf.* 226 kJ mol^{-1} for Sn–C bonds) [1]. Consequently, organolead(IV) halides decompose at room temperature, especially when exposes to light, although aryl derivatives are somewhat more stable than alkyl derivatives [2]. The decomposition of dialkyllead dihalides involves a redistribution reaction,

$$2R_2PbX_2 \rightarrow R_3PbX + RPbX_3$$

followed by reductive elimination of RX from the unstable monoorganolead derivative:

$$RPbX_3 \rightarrow PbX_2 + RX$$

These reactions hinder the synthesis of diorganolead(IV) complexes with anionic ligands. In particular, since the rates of the redistribution and reductive elimination reactions increase with the polarizability of the anion [3], reactions with soft anionic ligands very often lead to Pb(II) and $R_3Pb(IV)$ complexes instead of the $R_2Pb(IV)$ derivative.

As a continuation of our research into the coordination chemistry of organolead(IV) cations [4], here we report the results of reactions between dimethyl-, diphenyl- or triphenyllead(IV) derivatives and formylferrocene or acetylferrocene thiosemicarbazones (HTSCs, see Scheme 1). Metal

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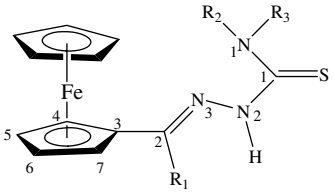
	R_1	R_2	R_3
HFTSC	H	H	H
HFMeTSC	H	H	CH_3
HFPhTSC	H	H	Ph
HFEtTSC	H	H	Et
HFMeMeTSC	H	CH_3	CH_3
HATSC	CH_3	H	H
HAMeTSC	CH_3	H	CH_3
HAPhTSC	CH_3	H	Ph
HAEtTSC	CH_3	H	Et
HAMeMeTSC	CH_3	CH_3	CH_3



Scheme 1. Thiosemicarbazones used in this work [F = formylferrocene; A = acetylferrocene; Me, Et, Ph = group on N(1)].

complexes of HTSCs are of interest because the delocalised π electron system of the thiosemicarbazone chain can transmit the electronic effects of the ferrocenyl radical [5,6], which may allow the use of the ferrocenylthiosemicarbazones as a chemical sensor. The reactions carried out in this work, which in some cases involved dephenylation or demethylation, led to the isolation of several new complexes of the starting organolead(IV) cations. These products were characterized structurally, and the redox behaviour was investigated.

2. Experimental

2.1. Instrumentation

Elemental analyses were performed on a Fisons EA1108CHNS-O microanalyser. Melting points (m.p.) were determined with a Büchi apparatus. Mass spectra were recorded in a Hewlett–Packard model 1100 MSD (ESI, methanolic or chloroform solution) or in a Micromass AUTOSPEC spectrometer (LSIMS, NBA matrix); the m/z values of metallated fragments are given for the isotopes ^{56}Fe, ^{208}Pb and ^{35}Cl. IR spectra were obtained using KBr discs on a Bruker IFS66V FT-IR spectrophotometer and are reported in cm^{-1}. The ^1H, ^{13}C and ^{207}Pb NMR spectra of DMSO-d_6 solutions were recorded on Bruker DPX 250, AMX 300 or AMX 500 spectrometers; chemical shifts in ppm were referred to tetramethylsilane using the solvent signal for ^1H and ^{13}C spectra and using a saturated dissolution of Ph_4Pb in $CDCl_3$ (−178.0 ppm) as external reference for ^{207}Pb spectra. HMQC and HMBC experiments were used for the assignment of signals. All the above physical measurements were performed by the RIAIDT services of the University of Santiago de Compostela (USC).

Cyclic voltammograms were obtained in dry CH_2Cl_2 (10^{-3} M solutions) with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte using a PAR Model 273 potentiostat/galvanostat, a saturated calomel reference electrode, a Pt wire as counter electrode, and a graphite disc as working electrode.

2.2. Materials

Thiosemicarbazide and silver acetate (both from Fluka), formyl- and acetylferrocene, 4-methyl-, 4-phenyl-, 4-ethyl-, 4-methyl- and 4,4-dimethyl-3-thiosemicarbazides, lead(II) iodide and triphenyllead(IV) chloride (all from Aldrich), bromine (from Merck), methyllithium (from Ega-Chemie), diphenyllead(IV) chloride and hydrochloric acid (from Panreac), iodomethane (from Probus); and acetic acid (from Analema); were all used as received. Solvents were of reagent grade. $Me_2Pb(OAc)_2$ was prepared as described in the literature [7], and $Ph_2Pb(OAc)_2$ and $[Ph_3Pb(OAc)]$ by stirring di- or triphenyllead(IV) chloride with silver acetate in methanol for 5 h; all three were characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. The acetylferrocene ligands were obtained by the method of Jayasree and Aravindakshan [8], and the formylferrocene ligands by the method of Wiles and Suprunchuk [9]. Some physical and spectroscopic properties of these compounds have been published elsewhere [5,10].

2.3. Synthesis of the complexes

Complexes derived from Ph_2PbCl_2 or $Ph_2Pb(OAc)_2$ were synthesized by mixing a suspension of one of these compound in methanol with a solution of the corresponding thiosemicarbazone in the same solvent. Metal:ligand mole ratio (1:1 or 1:2) did not influence the identity of the product; Table 1 lists the mole ratio giving the better yield, together with other experimental conditions and some physical properties of the complexes.

Reaction of $Ph_3Pb(OAc)$ lead to its dephenylation and the formation of the corresponding diphenyllead(IV) complexes (see below).

The reaction of HTSCs with $Me_2Pb(OAc)_2$ afforded Pb(II) complexes (Table 2), suggesting the occurrence of redistribution and reductive elimination.

Some syntheses are described below in detail as examples. Analogous information for the remaining complexes is included in Section 2.3S (here and hereafter, the suffix "S" indicates text, figures or tables included in the Supporting Information).

Caution! Lead is a highly toxic cumulative poison, and its compounds should be handled carefully [11].

Table 1
Reaction conditions for the synthesis of complexes derived from Ph_2PbCl_2 and $Ph_2Pb(OAc)_2$

Organolead(IV) Compound	Complex	Mole ratio M:L[a]	Reflux time (h)	Yield (%)	Colour	M.p. (°C)
Ph_2PbCl_2	$[Ph_2PbCl_2(HFTSC)_2]$	1:2	.	65	Red	177
	$[Ph_2PbCl_2(HFMeTSC)_2]$	1:2	8	57	Orange	197
	$[Ph_2PbCl_2(HFPhTSC)_2]$	1:2	12	40	Brown	176
	$[Ph_2PbCl_2(HFEtTSC)_2]$	1:2	.	54	Orange	179
	[Ph$_2$PbCl(FMeMeTSC)]	1:1	8	83	Brown	>250
	$[Ph_2PbCl_2(HATSC)_2]$	1:2	.	67	Orange	175
	$[Ph_2PbCl_2(HAMeTSC)_2]$	1:2	.	72	Orange	168
	$[Ph_2PbCl_2(HAPhTSC)_2]$	1:2	12	41	Brown	153
	$[Ph_2PbCl_2(HAEtTSC)_2]$	1:2	.	49	Orange	183
	$[Ph_2PbCl_2(HAMeMeTSC)_2]$	1:2	.	58	Red	169
$Ph_2Pb(OAc)_2$	$[Ph_2Pb(OAc)_2(HFTSC)_2]$	1:2	.	71	Orange	138
	$[Ph_2Pb(FMeTSC)(OAc)] \cdot MeOH$	1:1	8	72	Red	139
	$[Ph_2Pb(FEtTSC)(OAc)] \cdot MeOH$	1:1	16	46	Orange	120
	[Ph$_2$Pb(FMeMeTSC)(OAc)]	1:1	10	69	Red	214
	$[Ph_2Pb(OAc)_2(HATSC)_2] \cdot (CH_3CH_2)_2O$	1:2	.	38	Orange	113
	$[Ph_2Pb(OAc)_2(HAMeTSC)_2]$	1:2	.	33	Orange	143
	$[Ph_2Pb(OAc)_2(HAEtTSC)_2]$	1:2	8	39	Orange	105
	[Ph$_2$Pb(AMeMeTSC)(OAc)]	1:1	8	58	Red	148

[a] All the reactions were performed in both 1:1 and 1:2 mole ratio; only ratio giving the better yield is listed.

Table 2
Complexes derived from $Me_2Pb(OAc)_2$

Complex	Yield (%)	Colour	M.p. (°C)
[Pb(FTSC)$_2$]	36	Orange	205
[Pb(FMeTSC)$_2$]	30	Yellow	205
[Pb(FPhTSC)$_2$]	61	Orange	176
[Pb(FEtTSC)$_2$]	39	Yellow	204
[Pb(FMeMeTSC)$_2$]	74	Orange	>250
[Pb(ATSC)$_2$]	21	Orange	210
[Pb(AMeTSC)$_2$]	33	Yellow	222
[Pb(APhTSC)$_2$]	35	Orange	142
[Pb(AEtTSC)$_2$]	42	Yellow	218
[Pb(AMeMeTSC)$_2$]	38	Orange	186

2.3.1. Complexes derived from $[Ph_2PbCl_2]$

$[Ph_2PbCl_2(HATSC)_2]$. A suspension of Ph_2PbCl_2 (0.11 g, 0.25 mmol) in 15 mL of methanol was added dropwise, with stirring, to a solution of HATSC (0.15 g, 0.50 mmol) in 15 mL of the same solvent. The resulting solution was stirred for 12 h and then concentrated under reduce pressure until cloudy. After a further 12 h uncovered, the remaining solution afforded an orange solid that was filtered out and dried under reduced pressure. Yield 67%; m.p. 175 °C. Anal. Calc. for $C_{38}H_{40}N_6S_2Cl_2Fe_2Pb$: C, 44.1; H, 3.9; N, 8.1. Found: C, 43.5; H, 3.8; N, 7.5%. MS (electrospray), *m*/*z* (%): 698 (90) [M−HATSC−Cl], 662 (100) [M−ATSC−2Cl], 508 (31) [Pb(ATSC)], 301 (14) [HATSC]. IR: 3410s, 3284s, 3165w, *ν*(N–H); 1583vs, *ν*(C=N); 820m, *ν*(C=S). ^{1}H NMR: *δ*[N(2)*H*] 9.95s(1); *δ*[N(1)H$_2$] 8.09s(1), 7.65s(1); *δ*[C(20)*H*] 2.18s(3); *δ*[Ph$_2$Pb] (8.11d(2) H$_o$, 7.60t(2) H$_m$, 7.43t(1) H$_p$); [^3J(H–Pb)] 204.92 Hz. ^{13}C NMR: *δ*[C(1)] 177.6; *δ*[C(2)] 150.3; *δ*[C(3)] 83.0; *δ*[C(20)] 15.1; *δ*[Ph$_2$Pb] (170.1 C$_i$, 133.3 C$_o$, 129.4 C$_m$, 129.3 C$_p$); [^2J(C$_o$–Pb)] 127.0 Hz; [^3J(C$_m$–Pb)] 200.9 Hz. ^{207}Pb NMR: −506.9. Single crystals suitable for X-ray study were obtained by recrystallization from acetone.

[Ph$_2$PbCl(FMeMeTSC)]. A solution of HFMeMeTSC (0.15 g, 0.48 mmol) in 40 mL of hot methanol was added dropwise, with stirring, to a room-temperature suspension of Ph_2PbCl_2 (0.16 g, 0.48 mmol) in 15 mL of methanol. The mixture was refluxed for 8 h, stirred for a further 12 h, concentrated under reduced pressure until cloudy, and kept uncovered for 12 h. The brown solid obtained was filtered off and dried under vacuum. Yield 83%; m.p. >250 °C. Anal. Calc. for $C_{26}H_{26}N_3SClFePb$: C, 43.9; H, 3.7; N, 5.9. Found: C, 44.7; H, 3.7; N, 6.4%. MS (electrospray), *m*/*z* (%): 712 (2) [M+H], 676 (11) [M−Cl], 512 (100) [PbCl(FMeMeTSC-HNMe$_2$)], 314 (7) [FMeMeTSC]. IR: 1588s, *ν*(C=N); 822m, *ν*(C=S). ^{1}H NMR (predominant isomer): *δ*[N(1)*CH*$_3$] 3.28s(6); *δ*[C(2)*H*] 7.48s(1); *δ*[Ph$_2$Pb] 7.95d(2) H$_o$, 7.58t(2) H$_m$, 7.42t(1) H$_p$; [^3J(H–Pb)] 183.89 Hz. ^{13}C NMR: *δ*[C(1)] 169.7; *δ*[C(2)] 150.2; *δ*[C(3)] 74.3; *δ*[N(1)*CH*$_3$] 38.7; *δ*[Ph$_2$Pb] 165.8 C$_i$, 133.6 C$_o$, 130.0 C$_m$, 129.3 C$_p$. ^{207}Pb NMR: −509.0, −285.0.

2.3.2. Complexes derived from $[Ph_2Pb(OAc)_2]$ and $[Ph_3Pb(OAc)]$

$[Ph_2Pb(OAc)_2(HFTSC)_2]$. A freshly prepared solution of $Ph_2Pb(OAc)_2$ (0.26 mmol) in methanol (15 mL) was added dropwise, with stirring, to a solution of HFTSC (0.15 g, 0.52 mmol) in the same solvent (15 mL). After 12 h, half the solvent was removed under vacuum, and the remaining solution was left uncovered for 12 h. The resulting oil was broken under reduced pressure, affording an orange solid. Yield 71%; m.p. 138 °C. Anal. Calc. for $C_{40}H_{42}N_6O_4S_2Fe_2Pb$: C, 45.6; H, 4.0; N, 8.0. Found: C, 46.1; H, 4.0; N, 9.1%. MS (FAB, nitrobenzyl alcohol), *m*/*z* (%): 934 (2) [Ph$_2$Pb(FTSC)$_2$], 648 (100) [Ph$_2$Pb(FTSC)], 494 (65) [Pb(FTSC)], 287 (40) [HFTSC], 212 (22) [HFTSC-NHC(S)NH$_2$]. IR: 3419m, 3247m,br, 3155m,br, *ν*(N–H); 1599s, *ν*(C=N); 832sh, *ν*(C=S). ^{1}H NMR: *δ*[N(2)*H*] 11.18s(1); *δ*[N(1)*H*$_2$] 8.03s(1), 7.61s(1); *δ*[C(2)*H*] 7.87s(1);

δ[Ph_2Pb] (7.94d(2) H_o, 7.53t(2) H_m, 7.38t(1) H_p); δ[OAc] 1.84s(3); [^3J(H–Pb)] 197.42 Hz. ^{13}C NMR: δ[C(1)] 176.6; δ[C(2)] 143.2; δ[C(3)] 78.9; δ[Ph_2Pb] (167.6 C_i, 132.2 C_o, 129.6 C_m, 129.1C_p); δ[OAc] (171.2 C=O, 23.0 CH_3); [$^2J(C_o$–Pb)] 122.1 Hz; [$^3J(C_m$–Pb)] 183.1 Hz. ^{207}Pb NMR: −659.6.

[Ph_2Pb(FEtTSC)(OAc)]·MeOH. A freshly prepared solution of $Ph_2Pb(OAc)_2$ (0.48 mmol) in methanol (15 mL) was added dropwise, with stirring, to a solution of HFEtTSC (0.15 g, 0.48 mmol) in 10 mL of the same solvent. The mixture was refluxed for 16 h, and then stirred for a further 12 h. The remaining solution was left uncovered for 12 h, and the orange solid obtained was filtered off and dried under vacuum. Yield 46%; m.p. 120 °C. Anal. Calc. for $C_{29}H_{33}N_3O_3SFePb$: C, 45.4; H, 4.3; N, 5.5. Found: C, 44.8; H, 4.3; N, 5.6%. MS (FAB, nitrobenzyl alcohol), *m*/*z* (%): 676 (71) [M−MeOH−OAc], 522 (100) [Pb(FEtTSC)], 315 (30) [HFEtTSC], 212 (45) [HFEtTSC-NHC(S)NHEt]. IR: 3356m, *ν*(N–H); 1567sh, *ν*(C=N); 796sh, *ν*(C=S); 1602m, ν_{as}(COO); 1410m, ν_s(COO). ^{1}H NMR: δ[N(1)*H*] 7.24d(1); δ[N(1)CH_2] 3.42m(2); δ[N(1)CH_3] 1.21t(3); δ[C(2)*H*] 7.46s(1); δ[Ph_2Pb] (7.93d(2) H_o, 7.51t(2) H_m, 7.37t(1) H_p); δ[OAc] 1.74s(3); [^3J(H–Pb)] 189.14 Hz. ^{13}C NMR: δ[C(1)] 177.5; δ[C(2)] 149.3; δ[C(3)] 74.7; δ[N(1)CH_2] 38.4; δ[N(1)CH_3] 14.3; δ[Ph_2Pb] (166.4 C_i, 133.5 C_o, 129.6 C_m, 129.1 C_p); δ[OAc] (167.8 C=O, 23.4 CH_3); [$^2J(C_o$–Pb)] 122.6 Hz; [$^3J(C_m$–Pb)] 184.8 Hz. Single crystals suitable for X-ray study were obtained from methanol.

The same complex was obtained from $Ph_3Pb(OAc)$ as follows: a solution of triphenyllead(IV) acetate (0.48 mmol) in 15 mL of methanol was added dropwise to a solution of HFEtTSC (0.15 g, 0.48 mmol) in 15 mL of the same solvent. After 12 h of stirring, the solution was concentrated to half volume and the orange solid formed was isolated and dried under vacuum (yield 15%). Analytical data and physical and spectroscopic properties indicate that the solid is [Ph_2Pb(FEtTSC)(OAc)].

2.3.3. Complexes derived from [$Me_2Pb(OAc)_2$]

[Pb(FTSC)$_2$]. A freshly prepared solution of $Me_2Pb(OAc)_2$ (0.50 mmol) in 15 mL of methanol was added dropwise, with stirring, to a solution of HFTSC (0.14 g, 0.50 mmol) in the same solvent (25 mL). After 12 h stirring, the orange solid obtained was filtered out and dried under vacuum. Yield 36%; m. p. 205 °C. Anal. Calc. for $C_{24}H_{24}N_6S_2Fe_2Pb$: C, 37.0; H, 3.1; N, 10.8. Found: C, 36.6; H, 3.2; N, 10.7%. MS (electrospray), *m*/*z* (%): 1274 (10) [Pb_2(FTSC)$_3$], 781 (100) [M+H], 494 (81) [M-FTSC], 288 (17) [HFTSC+H], 287 (38) [HFTSC]. IR: 3466m, 3424s, 3373m, 3297m, *ν*(N–H); 1569vs, *ν*(C=N); 820m, br, *ν*(C=S). ^{1}H NMR: δ[N(1)H_2] 7.00s(2); δ[C(2)*H*] 8.22s(1). ^{13}C NMR: δ[C(1)] 173.1; δ[C(2)] 146.3; δ[C(3)] 80.1.

[Pb(ATSC)$_2$]. A freshly prepared solution of $Me_2Pb(OAc)_2$ (0.50 mmol) in 15 mL of methanol was added dropwise, with stirring, to a solution of HATSC (0.15 g, 0.50 mmol) in 25 mL of methanol. After stirring for 12 h, the orange solid obtained was filtered out and dried under reduced pressure. Yield 21%; m.p. 210 °C. Anal. Calc. for $C_{26}H_{28}N_6S_2Fe_2Pb$ requires: C, 38.7; H, 3.5; N, 10.4. Found: C, 38.8; H, 3.8; N, 10.4%. MS (electrospray), *m*/*z* (%): 1316 (9) [Pb_2(ATSC)$_3$], 809 (100) [M+H], 508 (57) [M−ATSC], 302 (6) [HATSC+H], 301 (2) [HATSC]. IR: 3483s, 3415s, 3364m, 3282m, *ν*(N–H); 1563vs, *ν*(C=N); 821m, br, *ν*(C=S). ^{1}H NMR: δ[N(1)H_2] 6.93s(2); δ[C(20)*H*] 2.13s(3). ^{13}C NMR: δ[C(1)] 170.2; δ[C(2)] 152.9; δ[C(3)] 84.3; δ[C(20)] 16.1.

2.4. X-ray crystallography

Crystal data were collected at room temperature on a Bruker SMART CCD 1000 diffractometer [12] using graphite-monochromated Mo Kα radiation (wavelength 0.71073 Å). The structures were solved using direct methods followed by normal difference Fourier techniques. The hydrogen atoms were included in the model at ideal positions. Full-matrix least-squares refinement was performed treating the non-H atoms anisotropically. The atomic scattering factors used were those provided with SHELX-97 [13]. Other programs used were ORTEP-3 [14] and PLATON-98 [15]. Crystal and refinement data for the compounds are listed in Table 3.

3. Results and discussion

3.1. Synthesis of the complexes

3.1.1. Reactions of Ph_2PbX_2 (X = Cl, OAc)

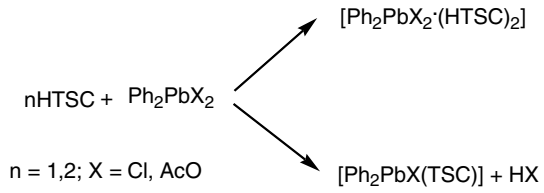
The reactions of Ph_2PbX_2 (X = Cl, OAc) with HTSCs in methanol afforded either 1:2 adducts [Ph_2PbX_2(HTSC)$_2$] or 1:1 complexes in which an X^- ligand had been replaced by TSC^- (Scheme 2).

The stoichiometry of the reaction mixture (all reactions were performed with both 1:1 and 1:2 metal:HTSC ratios) had no influence on the identity of the product, which was generally unique, but it did affect yield, 1:2 adducts being obtained in greater yield with 1:2 ratio and 1:1 complexes with 1:1 ratio. It is possible that complexes of both stoichiometries exist in solution, and that which is isolated depends on their relative solubilities. Only in the reactions of $Ph_2Pb(OAc)_2$ with HFPhTSC and HAPhTSC did failure to isolate a pure product suggest that the solids obtained might be a mixture of 1:1 and 1:2 complexes, a result that may perhaps have been due to the deactivating influence of the HTSC phenyl on its carbothioamide group.

The singular displacement of a Cl^- ligand by HFMeMeTSC deserves a comment. In this HTSC, both the N(1)H_2 hydrogens had been replaced by methyl groups. This double substitution eliminates the intramolecular N(1)–H···N(3) hydrogen bond, thereby allowing free rotation about the C(1)–N(2) bond and facilitating the N(3),S-coordination that is suggested by spectroscopic data (*vide infra*). It therefore seems possible that in this reaction the

Table 3
Crystallographic data for the complexes studied by X-ray diffraction

	$[Ph_2PbCl_2(HFMeTSC)_2]$	$[Ph_2PbCl_2(HATSC)_2]$	$[Ph_2PbCl_2(HAMeTSC)_2]\cdot 2MeOH$	$[Ph_2PbCl_2(HAEtTSC)_2]\cdot 2(CH_3)_2CO$	$[Ph_2Pb(OAc)(FMeTSC)]\cdot MeOH$	$[Ph_2Pb(OAc)(FEtTSC)]\cdot MeOH$
Empirical formula	$C_{38}H_{40}Fe_2N_6Cl_2S_2Pb$	$C_{38}H_{40}Fe_2N_6Cl_2S_2Pb$	$C_{42}H_{52}Fe_2N_6Cl_2O_2S_2Pb$	$C_{48}H_{60}Fe_2N_6Cl_2O_2S_2Pb$	$C_{28}H_{31}FeN_3O_3SPb$	$C_{29}H_{33}FeN_3O_3SPb$
Formula weight	1034.67	1034.67	1126.81	1206.93	752.66	766.68
Colour, habit	Red, prism	Red, prism	Red, needle	Red, prism	Red, prism	Red, prism
Crystal size	$0.39\times0.13\times0.08$ mm	$0.46\times0.37\times0.15$ mm	$0.43\times0.08\times0.06$ mm	$0.55\times0.49\times0.17$ mm	$0.20\times0.18\times0.16$ mm	$0.55\times0.30\times0.22$ mm
Crystal system, space group	Triclinic,$P\bar{1}$	Monoclinic, $P2(1)/n$	Monoclinic, $P2(1)/c$	Monoclinic, $P2(1)/c$	Orthorhombic, $P212121$	Orthorhombic, $P212121$
Unit cell dimensions						
a (Å)	9.0796(15)	8..9140(15)	11.4938(5)	14.948(3)	10.405(2)	10.5052(14)
b (Å)	9.6305(16)	7.7592(13)	16.0036(7)	11.0324(18)	15.200(3)	15.633(2)
c (Å)	12.851(2)	27.606(5)	12.3901(5)	15.885(3)	18.138(3)	18.344(3)
α (°)	104.269(3)	–	–	–	–	–
β (°)	99.181(3)	94.692(3)	92.608(3)	98.213(3)	–	–
γ (°)	112.391(2)	–	–	–	–	–
Volume	965.8(3) Å^3	1903.0(6) Å^3	2276.70(17) Å^3	2592.8(7) Å^3	2868.6(9) Å^3	3012.6(7) Å^3
Z; Calculated density	1; 1.779 Mg/m^3	2; 1.806 Mg/m^3	2; 1.644 g/m^3	2; 1.546 Mg/m^3	4, 1.743 Mg/m^3	4, 1.690 Mg/m^3
Absorption coefficient	5.372 mm^{-1}	5.452 mm^{-1}	4.568 mm^{-1}	4.017 mm^{-1}	6.473 mm^{-1}	6.165 mm^{-1}
T (K)	293	293	293	293	293	293
F (000)	510	1020	1124	1212	1472	1504
Reflections collected/ unique (R_{int})	10,953/3931 (0.0230)	11,130/3875 (0.0212)	34,619/5644 (0.0482)	15,965/5301 (0.0237)	12,528/5277 (0.0301)	11,422/5438 (0.0174)
Final R indices $[I > 2\text{sigma}(I)]$	$R_1 = 0.0170$	$R_1 = 0.0249$	$R_1 = 0.0289$	$R_1 = 0.0241$	$R_1 = 0.0269$	$R_1 = 0.0270$
	$wR_2 = 0.0393$	$wR_2 = 0.0581$	$wR_2 = 0.0517$	$wR_2 = 0.0602$	$wR_2 = 0.0506$	$wR_2 = 0.0690$



Scheme 2.

displacement of the Cl^- may have been facilitated by prior coordination of HFMeMeTSC in a chelated mode. No success was achieved when the displacement of Cl^- by other HTSC ligands was attempted by performing the reaction additionally in a basic medium.

That most of 1:1 complexes derived from $Ph_2Pb(OAc)_2$ rather than Ph_2PbCl_2 may have been due to acetate being more basic than chloride, which must have aided deprotonation of the thiosemicarbazone.

3.1.2. Reactions of $Ph_3Pb(OAc)$ and $Me_2Pb(OAc)_2$

When the starting organolead compound was $Ph_3Pb(OAc)$, dephenylation occurred:

$$Ph_3Pb(OAc) + HTSC \rightarrow [Ph_2Pb(OAc)(TSC)] + HPh \quad (1)$$

Yields, however, were very low (see Section 2.3.2).

The reactions of $Me_2Pb(OAc)_2$ with HTSCs afforded Pb(II) complexes almost instantaneously, even at low temperature and in the absence of light, showing that the Pb–Me bond is less stable than the Pb–Ph bond. It may be assumed that after substitution of TSC^- for AcO^- there occurred a redistribution reaction,

$$2[Me_2Pb(TSC)_2] \rightarrow [MePb(TSC)_3] + [Me_3Pb(TSC)] \quad (2)$$

followed by reductive elimination from the monomethyl complex:

$$[MePb(TSC)_3] \rightarrow TSC - Me + [Pb(TSC)_2] \quad (3)$$

(see Section 1). However, since this process can afford at most a 50% yield of the lead(II) complex, the fact that yields of 61% and 74% were obtained with HFPhTSC and HFMeMeTSC (see Table 2) shows that, at least in these cases, some alternative decomposition pathway must also have been operative. To investigate this, the ^1H NMR spectrum of a 1:1 solution of $Me_2Pb(OAc)_2$ and HFTSC in CD_3OD was monitored during several days. Within 24 h, the organometallic signal at 2.19 ppm [$^2J(^1H–^{207}Pb) = 150$ Hz)] was replaced by three new peaks at 0.72 ppm [$^2J(^1H–^{207}Pb) = 62$ Hz], 1.37 ppm [$^2J(^1H–^{207}Pb) = 81$ Hz] and 2.46 ppm (no coupling constant could be measured for this last signal). Although ^1H NMR data for methyllead(IV) derivatives are somewhat scarce, it seems that the $^2J(^1H–^{207}Pb)$ coupling constant of Me_4Pb lies close to 60 Hz, those of trimethyllead derivatives between 70 and 90 Hz, and those of dimethyllead(IV) compounds near 150 Hz [2]. Accordingly, those measured in the $Me_2Pb(OAc)_2$/HFTSC reaction after 24 h probably belong to Me_4Pb, Me_3Pb and MePb, respectively. Simultaneously with these spectroscopic changes, a precipitate forms that is presumably the Pb(II) complex, and a new signal appears at 2.70 ppm that may plausibly belong to the FTSC-Me. These data not only support reactions 2 and 3, but also indicate that $[Me_3Pb(FTSC)]$ undergoes the redistribution reaction [2]:

$$2[Me_3Pb(FTSC)] \rightarrow Me_4Pb + [Me_2Pb(FTSC)_2] \quad (4)$$

making the overall process

$$3[Me_2Pb(FTSC)_2] \rightarrow Me_4Pb + 2[Pb(FTSC)_2] + 2FTSC - Me \quad (5)$$

and accounting for the observed yields of the HFPhTSC and HFMeMeTSC complexes.

3.2. X-ray structures of the complexes

Table 4 lists selected bond lengths and angles in the complexes studied crystallographically, and Figs. 1 and 2 show the structures and numbering schemes of two examples.

In all the compounds derived from Ph_2PbCl_2 {$[Ph_2PbCl_2(HFMeTSC)_2]$, $[Ph_2PbCl_2(HATSC)_2]$, $[Ph_2PbCl_2(HAMeTSC)_2]\cdot 2MeOH$ and $[Ph_2PbCl_2(HAEtTSC)_2]\cdot 2(CH_3)_2CO$}, an all-*trans* octahedral arrangement is adopted by the six ligands, namely the two phenyl groups, the two chloride ligands and the sulphur atoms of the two HTSC ligands (see Fig. 1 for $[Ph_2PbCl_2(HATSC)_2]$ and Fig. 1S for the other adducts). The bond angles are close to their ideal values (see Table 4). In $[Ph_2PbCl_2(HATSC)_2]$ the Pb-S distance, 2.8966(10) Å, is clearly longer than the 2.819(2) Å observed in $[Ph_2PbCl_2(HSTSC)_2]$ (HSTSC = salicylaldehyde thiosemicarbazone), a similar centrosymmetric adduct [4c], suggesting that HATSC is less basic than HSTSC. The Pb-Cl distance in $[Ph_2PbCl_2(HATSC)_2]$, 2.7471(9) Å, is also longer than in the HSTSC adduct [2.715(3) Å], but clearly shorter than in polymeric Ph_2PbCl_2 [2.795(6) Å], in which all the Cl^- anions are bridging ligands [16]. The C(1)–S(1) bond length, 1.716(4) Å, is greater than in HATSC [1.693(3) Å] [17], suggesting partial evolution to the thiol form in the adduct. The other distances in the thioamide group are not significantly changed. The thiosemicarbazone chain C(2)N(3)N(2)C(1)S(1)N(1) is practically planar (rms = 0.0823) and retains the same configuration as in the free ligand, E about both the C(1)–N(2) and C(2)–N(3) bonds. The *E* configuration about C(1)–N(2) allows the formation of two intramolecular hydrogen bonds, N(1)–H(1A)···N(3) [N(1)···N(3) = 2.639(4), N(1)–H(1A) = 0.86, H(1A)···N(3) = 2.30 Å; N(1)–H(1A)···N(3) = 104.0°] and N(2)–H(2)···Cl(1) [N(2)···Cl(1) = 3.209(3), N(2)–H(2) = 0.86, H(2)···Cl(1) = 2.71 Å; N(2)–H(2)···Cl(1) = 118.0°]. This intramolecular hydrogen-bonding scheme is common to all four Ph_2PbCl_2 adducts (see Table 1S). In $[Ph_2PbCl_2(HATSC)_2]$ there is additionally an intermolecular hydrogen bond [N(1)···Cl(1)$^{\#}$ = 3.273(3), N(1)–H(1B) = 0.86, H(1B)···Cl(1)$^{\#}$ =

Table 4
Selected bond lengths (Å) and angles (°) in the complexes

	$[Ph_2PbCl_2(HFMeTSC)_2]$	$[Ph_2PbCl_2(HATSC)_2]$	$[Ph_2PbCl_2(HAMeTSC)_2]\cdot 2MeOH$	$[Ph_2PbCl_2(HAEtTSC)_2]\cdot 2(CH_3)_2CO$	$[Ph_2Pb(OAc)(FMeTSC)]\cdot MeOH$	$[Ph_2Pb(OAc)(FEtTSC)]\cdot MeOH$
Pb(1)–S(1)	2.8824(7)	2.8966(10)	2.8522(10)	2.8214(9)	2.5397(17)	2.5367(14)
Pb(1)–Cl(1)	2.6768(7)	2.7471(9)	2.7229(10)	2.7063(8)	–	–
Pb(1)–C(21)	2.190(2)	2.183(3)	2.185(3)	2.188(3)	2.194(6)	2.194(5)
Pb(1)–C(15)	–	–	–	–	2.187(6)	2.197(6)
Pb(1)–N(3)	–	–	–	–	2.479(4)	2.477(4)
Pb(1)–O(1)	–	–	–	–	2.326(4)	2.318(4)
Pb(1)–O(2)	–	–	–	–	2.923(5)	2.911(5)
S(1)–C(1)	1.704(2)	1.716(4)	1.709(4)	1.709(3)	1.755(6)	1.757(6)
C(1)–N(1)	1.319(3)	1.309(5)	1.303(5)	1.306(4)	1.343(7)	1.352(7)
C(1)–N(2)	1.338(3)	1.343(4)	1.352(5)	1.344(4)	1.313(7)	1.297(7)
N(1)–C(13)	1.444(4)	–	1.456(5)	1.458(5)	1.443(8)	1.449(10)
N(2)–N(3)	1.386(3)	1.395(4)	1.390(4)	1.387(3)	1.381(7)	1.375(6)
N(3)–C(2)	1.284(3)	1.293(4)	1.286(5)	1.285(4)	1.287(7)	1.292(7)
C(2)–C(3)	1.436(3)	1.471(5)	1.461(5)	1.467(4)	1.450(8)	1.447(7)
S(1)–Pb(1)–Cl(1)	98.770(19)	89.49(3)	92.81(3)	91.57(3)	–	–
Cl(1)–Pb(1)–C(21)	90.43(7)	90.24(9)	90.34(10)	90.81(9)	–	–
Cl(1)–Pb(1)–S(1)$^{\#1}$	81.230(19) (*a*)	90.51(3) (*b*)	87.19(3) (*a*)	88.43(3) (*c*)	–	–
S(1)–Pb(1)–N(3)	–	–	–	–	73.66(14)	73.55(10)
O(1)–Pb(1)–O(2)	–	–	–	–	47.86(15)	48.23(14)
S(1)–Pb(1)–O(1)	–	–	–	–	79.85(13)	79.03(11)
N(3)–Pb(1)–O(2)	–	–	–	–	158.58(17)	159.25(13)
C(15)–Pb(1)–C(21)	–	–	–	–	145.8(2)	143.55(19)

$^{\#1}$(*a*) $-x+1, -y, -z$; (*b*) $-x, -y, -z$; (*c*) $-x+1, -y+1, -z$.

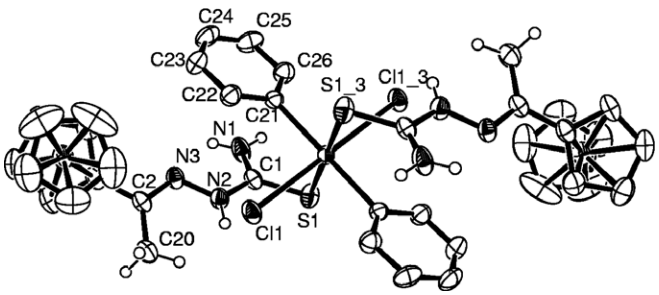


Fig. 1. ORTEP drawing of $[Ph_2PbCl_2(HATSC)_2]$, showing the molecular structure and the labelling scheme used.

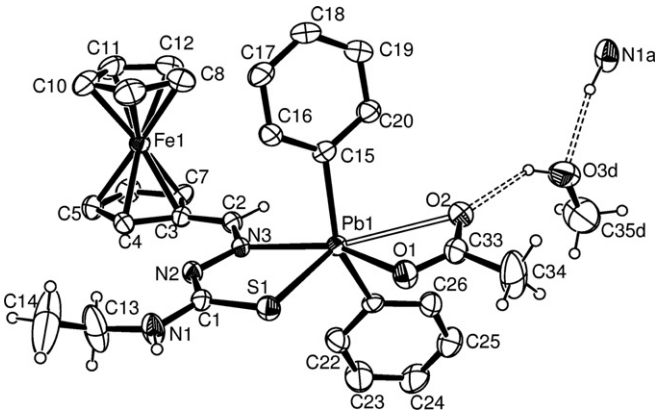


Fig. 2. ORTEP drawing of $[Ph_2Pb(OAc)(FEtTSC)]\cdot MeOH$, showing the molecular structure, the labelling scheme used, and the intermolecular hydrogen bonds that connect the molecules of complex via the methanol molecule.

2.49 Å; N(1)–H(1B)···Cl(1)$^{\#}$ = 151.8°; $^{\#} = x, y-1, z$] that links the molecules along the *y*-axis. A similar interaction associates the molecules along the *z*-axis in $[Ph_2PbCl_2(HAEtTSC)_2]\cdot 2(CH_3)_2CO$, in which the occluded acetone molecules take no part in the hydrogen bonding. By contrast, the intermolecular interactions are more complex in $[Ph_2PbCl_2(HAMeTSC)_2]\cdot 2MeOH$ because the MeOH molecules do participate in the hydrogen bond network. In $[Ph_2PbCl_2(HFMeTSC)_2]$ there are no intermolecular interactions (see Table 1S).

The two complexes derived from $Ph_2Pb(OAc)_2$ that were studied by X-ray diffractometry, $[Ph_2Pb(OAc)(FEtTSC)]\cdot MeOH$ and $[Ph_2Pb(OAc)(FMeTSC)]\cdot MeOH$, have similar structures (Figs. 2 and 2S). The metal again has coordination number six (or 5 + 1, see below), bonding to the two phenyl groups, one N(3),S(1)-coordinated thiosemicarbazonato ligand, and one anisobidentate acetate [Pb(1)–O(1) = 2.318(4), Pb(1)–O(2) = 2.911(5) Å in $[Ph_2Pb(OAc)(FEtTSC)]\cdot MeOH$]. Although the longer Pb–O distance exceeds all the acetate–diphenyllead(IV) distances reported hitherto [18], it is well short of the sum of the van der Waals radii, 3.5 Å [19]. With this weak interaction included, the metal has coordination number six and possesses a very distorted octahedral environment with the phenyl groups apical. The C–Pb–C bond angle, 143.55(19)°, differs widely from the ideal 180°, and the small bite of the ligands make the equatorial angles narrower than 90°. Nevertheless, the equatorial fragment [C(3)C(2)N(3)N(2)C(1)S(1)N(1)C(13)Pb(1)O(1)O(2)C(33)] is practically planar (rms = 0.0617).

Deprotonation and metallation change the thiosemicarbazide moiety in the usual ways [20]. Thus in $[Ph_2Pb(OAc)(FMeTSC)]\cdot MeOH$ the C(1)–S(1) bond is longer than in the corresponding adduct [1.755(6) as against 1.704(2) Å; see Table 4] in accordance with the greater evolution of the ligand towards the thiol form, and the configuration about the N(2)–C(1) bond is *Z* instead of *E* to allow the observed N(3),S-chelation. There are no significant differences in Pb–C bond length between adducts and complexes.

Though not bound to the metal, the methanol links the molecules of the $FRTSC^-$ complexes via two intermolecular hydrogen bonds (see Fig. 2 and Table 1S), acting as an acceptor for the N(1)–H(1) of one molecule [N(1)–H(1)···O(3D)], and as a donor for the weakly coordinated O atom of the acetato ligand of a neigbouring molecule [O(3D)–H(3D)···O(2)$^{\#}$].

3.3. IR spectroscopy

The main IR bands (see Section 2) were identified on the basis of data for similar lead compounds [7] and ligands [8,9]. Additional bands close to 1470, 1100, 1000, 820 and 480 cm^{-1} are essentially due to ferrocenyl group vibrations, although in several cases they include contributions from the thiosemicarbazone group [6].

In comparison with the spectra of the free HTSCs, those of all the $[Ph_2PbCl_2(HTSC)_2]$ compounds show slight shifts in the ν(N–H) bands (probably due to differences in the hydrogen bond network), in ν(C=S) (which is also less intense), and in ν(C=N). This common shift pattern suggests that in all these adducts the HTSC ligand has the same coordination mode, which the X-ray data for the HFMeTSC, HATSC, HAMeTSC and HAEtTSC derivatives show to be monodentate coordination through the sulphur atom. The HTSC bands have similar positions in the spectra of the $[Ph_2Pb(OAc)_2(HTSC)_2]$ compounds, suggesting that the HTSC ligand is also S-coordinated in these adducts. It is likewise plausible that these latter compounds, like the chloride derivatives, have an all-*trans* octahedral structure, with monodentate OAc^- ligands; but we were unable to test this hypothesis by conclusive identification of ν_{as}(COO) and ν_{sym}(COO).

The deprotonation of HTSC makes the 3400–3000 cm^{-1} region of the spectra of the $[Ph_2PbX(TSC)]$ and $[Ph_2Pb(TSC)_2]$ compounds much simpler than in the case of the neutral HTSC adducts. The spectra of $[Ph_2Pb(FMeMeTSC)(OAc)]$ and $[Ph_2PbCl(FMeMeTSC)]$ are practically identical except for the two strongest and broadest bands of the acetate, located at 1587 and 1387 cm^{-1}, which are attributed to ν_{as}(COO) and ν_{sym}(COO). This coincidence supports the proposal that the TSC^- ligands of these

compounds probably share the S,N-coordination found by the X-ray study of [Ph_2Pb(FMeTSC)(OAc)] and [Ph_2Pb(FEtTSC)(OAc)]. Similarly, in the spectra of all four [Ph_2Pb(TSC)(OAc)] compounds ν_{as}(COO) and ν_{sym} (COO) lie at positions in keeping with the anisobidentate OAc^- coordination [21] shown by the X-ray study to be present in [Ph_2Pb(FMeTSC)(OAc)] and [Ph_2Pb(FEtTSC)(OAc)]. The coordination number of the metal in these complexes, 6 (or 5 + 1), would also be attained in [Ph_2PbCl(FMeMeTSC)] if these molecules were associated in dimers by double Cl^- bridges. Such association would be in keeping with the strong, broad band observed at 190 cm^{-1} in the spectrum of this compound, but is not supported by the mass spectrum (see below), and the structural diversity of diphenyllead(IV) complexes of thiosemicarbazones [4c] therefore means that a monomeric structure cannot be ruled out.

The [$Pb(TSC)_2$] compounds, too, have spectra in which the positions of ν(C=N) and ν(C=S) suggest S,N-coordination by TSC^-. The scant solubility of these compounds suggests a polymeric structure, which could come about through the formation of Pb–S···Pb bridges similar to those found in [Pb(4ML)(SCN)] (4ML = 2-acetylpyridine-^4N-methylthiosemicarbazonato) [22].

3.4. Mass spectrometry

Since the FAB spectra of the [Ph_2PbCl_2(HTSC)$_2$] compounds only show fragments of the HTSC ligand, these compounds were also studied using ESI; the main metallated fragments are listed in Sections 2.3 and 2.3S. In all cases the highest-mass ion resulted from loss of a Cl^- and a thiosemicarbazone ligand by the initial adduct, and this peak was always of significant intensity, although the base peak always corresponded to the [M−2Cl−TSC] ion.

The ESI spectrum of [Ph_2PbCl(FMeMeTSC)] shows no multimetallated fragments suggestive of association in dimers in either methanol or chloroform. The highest-mass ion is the protonated molecular ion, which appears with low intensity (2%) at *m/z* 712. The base peak corresponds to a fragment with *m/z* 512 that was identified as the [PbCl(FMeMeTSC-HNMe_2)] ion. The formation of this fragment, which amounts to a reductive elimination that has also been observed in the spectra of other diphenyllead(IV) thiosemicarbazonates [4b], reflects the weakness of Pb–C bonds [1].

The FAB spectra of the complexes of general formula [$Ph_2Pb(OAc)_2$(HTSC)$_2$] all show a [Ph_2Pb(TSC)] fragment indicative of loss of the acetate ligands and one HTSC ligand. As in the cases of the chloride derivatives, dephenylation also occurs, giving the [Pb(TSC)] ion. The absence of metallated fragments containing the acetate group is explained by the FAB spectra of the [Ph_2Pb(OAc)(TSC)] complexes, which show Pb–OAc to be their weakest bond. Ready loss of the OAc^- group from acetate/thiosemicarbazonate complexes has previously been observed under ESI [4b]. In spite of this tendency, the FAB spectra of three of the four [Ph_2Pb(OAc)(TSC)] complexes also show a weak peak ascribable to the molecular ion minus any solvating methanol. The other main lead-bearing fragments are [PhPb(TSC)] and [Pb(TSC)].

3.5. NMR spectroscopy

The most relevant signals in the ^1H, ^{13}C and ^{207}Pb NMR spectra of the complexes in DMSO-d_6 solution are listed in Sections 2.3 and 2.3S. The poor solubility of these compounds precluded measurements in less coordinating solvents.

In the ^1H and ^{13}C NMR spectra of the adducts [Ph_2PbCl_2(HTSC)$_2$], the HTSC signals lie at the same positions as in the spectra of the free ligands [5,10]. Also the chemical shifts and coupling constants of the signals belonging to the organometallic moiety are practically identical to those of free Ph_2PbCl_2 in DMSO-d_6 solution {δ (ppm) 8.13 (H_o), 7.59 (H_m), 7.42 (H_p); $^3J(^1H–^{207}Pb)$ 205.9 Hz; for the ^{13}C NMR parameters, see [23]}. The δ ^{207}Pb values {e.g. −506.9 ppm for [Ph_2PbCl_2(HATSC)] and −506.6 ppm for [Ph_2PbCl_2(HFMeTSC)]} are also quite similar to the chemical shift of the free acceptor in the same solvent (−508.4 ppm in 2.10^{-2} M solution). All this suggests that DMSO-d_6 molecules, due to their donor capacity and their excess in solution, displace the thiosemicarbazone ligands, giving the complex [Ph_2PbCl_2-(DMSO)$_2$] [24] plus free HTSC.

The ^1H and ^{13}C NMR spectra of [Ph_2PbCl(FMeMeTSC)] are more complex, especially in the region of the phenyl and ferrocenyl bands. Several species appear to be present, but only the signals associated with one of the major ones, designated arbitrarily as **a**, were identified (by means of $^1H–^{13}C$ HMQC and HMBC experiments; see the Experimental Part). In the ^1H NMR spectrum the absence of a N(2)–H signal confirms the deprotonation of the thiosemicarbazone ligand. The ^{13}C NMR spectrum shows C(1) (169.7 ppm) to be more shielded than in the free HFcMeMeTSC (180.0 ppm [5]), which is in keeping with evolution to the thiol form, while C(2) is deshielded (150.2 ppm vs. 144.7 ppm in free HFMeMeTSC). All these changes are compatible with coordination of the thiosemicarbazone via the S and N(3) atoms. In addition, some of the ferrocenyl carbons are deshielded by as much as 5 ppm with respect to the free ligand, suggesting that the effects of coordination are transmitted from the thiosemicarbazone chain to this group. The ^{207}Pb NMR spectrum shows two signals, at −509.0 and −285.0 ppm; the upfield location is practically that of [Ph_2PbCl_2(DMSO)$_2$] (see above). In view of this, it seems plausible that in DMSO the complex undergoes the process:

$$2Ph_2PbCl(FMeMeTSC) + 2DMSO \rightarrow [Ph_2PbCl_2(DMSO)_2] + Ph_2Pb(FMeMeTSC)_2]$$

This would explain the presence of more than one set of Ph_2Pb signals in the ^1H and ^{13}C NMR spectra, and the

signal at −509.0 ppm in the ^{207}Pb NMR spectrum. Also, the difference between the coordination spheres of [Ph_2Pb-$Cl_2(DMSO)_2$] and [$Ph_2Pb(FMeMeTSC)_2$], with O and Cl donors in one and N and S donors in the other, makes it reasonable for the ^{207}Pb NMR signal of the latter to lie 224 ppm downfield from that of the former, since Pb is deshielded more by N-binding than by O-binding, and more still by S-binding [25,26]. The complexity of the ferrocenyl signals suggests that the two $FMeMeTSC^-$ ligands of [$Ph_2Pb(FMeMeTSC)_2$] may not be equivalent, or that the conformations of these ligands are not the same in all molecules.

The complexes derived from $Ph_2Pb(OAc)_2$ are poorly soluble even in DMSO, which in some cases precluded the recording of the ^{13}C and ^{207}Pb NMR spectra. However, for [$Ph_2Pb(OAc)_2(HFTSC)_2$] all the spectra were obtained. Although the ^{1}H and ^{13}C signals of the HFTSC ligand are practically at the same positions as in the spectra of free HFTSC [5], those of the Ph_2Pb moiety (see Section 3.2) differ slightly from those of $Ph_2Pb(OAc)_2$ in DMSO-d_6 (167.0 ppm, C_i; 134.5 ppm, C_o, 132.1 ppm, C_m; 130.0 ppm, C_p, $^2J_{C_o}$–Pb = 125 Hz, $^3J_{C_m}$–Pb = 206 Hz), and the ^{207}Pb nucleus is more deshielded in the complex (−659.6 ppm) than in $Ph_2Pb(OAc)_2$ (−858.0 ppm in 2.10^{-2} M solution; note that, as Fig. 3S shows, this parameter is practically independent of concentration, which rules out any association in solution). This deshielding, which is coherent with partial permanence of the S atom in the coordination sphere of the metal [26], is even more pronounced in [$Ph_2Pb(FMeTSC)(OAc)]\cdot MeOH$ (δ ^{207}Pb = −532.0 ppm) and [$Ph_2Pb(FMeMeTSC)(OAc)$] (δ ^{207}Pb = −530.0 ppm), in which the deprotonated ligand probably remains N(3),S-coordinated in solution.

The solubility of the [$Pb(TSC)_2$] complexes in DMSO-d_6, though very poor, did allow the recording of ^{1}H and ^{13}C NMR spectra in all cases, though not always with a good signal to noise ratio. In all the cases, both spectra confirm the presence of deprotonated N,S-coordinated ligands (see Sections 3.2 and 3.2S).

3.6. Cyclic voltammetry

In spite of the poor solubility of these complexes, it was possible to investigate the electrochemical behaviour of both a 1:2 and a 1:1 Ph_2Pb complexes of HFMeTSC in CH_2Cl_2 solution (see Table 5). The cyclic voltammograms were recorded in the potential range in which ferrocene undergoes redox processes. Like that of the free ligand [5], they reflect quasi-reversible redox processes {Fig. 3 shows that of [$Ph_2Pb(FMeTSC)(OAc)]\cdot MeOH$}. In each case, only one redox specie seems to be present, and like ferrocenyl thiosemicarbazonates of gold(III) [5], it has an $E_{1/2}$ value that is more positive than that of free HFMeTSC. This $E_{1/2}$ shift may be ascribed [27] to the inductive effect of the coordinated lead: coordination reduces the electron charge on the TSC chain and, via the chain, that of the ferrocenyl Fe(II) centre, making its oxidation more difficult. This interpretation, which assumes "communication" between the thiosemicarbazone and ferrocenyl moieties is supported by a recent theoretical study [6], and is in keeping with the positive $E_{1/2}$ shift being larger for [$Ph_2Pb(FMeTSC)(OAc)]\cdot MeOH$ than for [$Ph_2PbCl_2(HFMeTSC)_2$], since more electron charge should be transferred to the lead centre from N,S-bound $FMeTSC^-$ anion than from neutral S-bound HFMeTSC ligand. It thus seems that the redox "tail" of this type of thiosemicarbazone is sensitive not only to coordination by metals but also to the coordination mode.

Table 5
Electrochemical data (mV) for selected complexes

	$E_{1/2}$	Ref.
HFMeTSC	0.584	[5]
[$Ph_2PbCl_2(HFMeTSC)_2$]	0.604	This work
[$Ph_2Pb(FMeTSC)(OAc)]\cdot MeOH$	0.626	This work

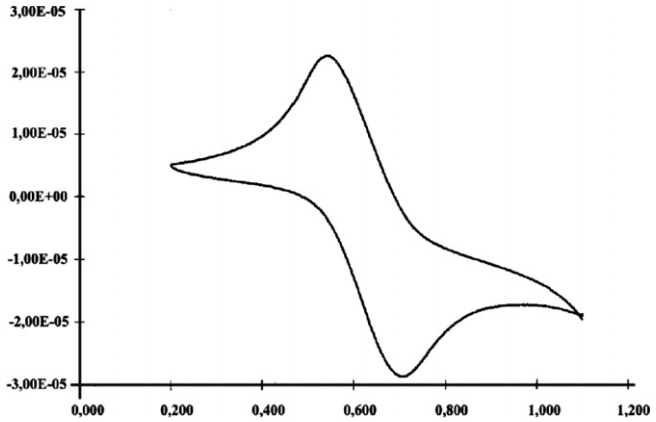


Fig. 3. Cyclic voltammogram of [$Ph_2Pb(FMeTSC)(OAc)]\cdot MeOH$.

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Appendix A. Supplementary material

1CCDC 631406,631407, 631408, 631409, 631410 and 631411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary

data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2007.01.049.

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