Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 358 (2005) 555–564
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Antisymbiosis. Preferential coordination of anionic oxygen versus neutral sulfur donor atoms of methylsulfanyl- or methylsulfinyl-acetato, 2-benzoato and 2-phenolato to the *cis*-$Pt^{II}(PPh_3)_2$ and Pt^{II}(dppe) residues

Laura Battan [a], Serena Fantasia [a], Mario Manassero [b,*], Alessandro Pasini [a,*], Mirella Sansoni [b]

[a] *Dipartimento di Chimica Inorganica, Metallorganica e Analitica, via Venezian 21, 20133 Milano, Italy*
[b] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, via Venezian 21, 20133 Milano, Italy*

Received 13 May 2004; accepted 22 September 2004
Available online 21 November 2004

Abstract

The interaction of an excess of the title ligands L^- with the *cis*-Pt(phos)$_2$ moieties gives compounds **a**–**b** *cis*-[Pt(L-*O*)$_2$(phos)$_2$] (**a**, phos = P(Ph)$_3$; **b**, phos = 1/2 dppe), in which *O*- is preferred to *S*-coordination. Such preference is confirmed by the fact that the same products are obtained by reaction of excess of L^- with the previously reported **a**–**d** complexes [Pt(L-*O,S*)(phos)$_2$]$^+$, (**c**, phos = PPh$_3$, **d**, phos = 1/2 dppe), for which chelate ring opening occurs with rupture of Pt–S rather than Pt–O bonds. Compound **a** can be obtained also by oxidative addition of HL to [Pt(PPh$_3$)$_3$]. The Pt–O bonds in compounds **a**–**d** are stable towards substitution by Me_2SO, pyridine and tetramethylthiourea. Substitution of L's occurs with *N*,*N*′-diethyldithiocarbamate, which forms a very stable chelate with Pt(II). Thiourea and *N*,*N*′-dimethylthiourea also react, because they give rise to cyclometallated products [Pt(phos)$_2$(*N*RC(*S*)NHR)]$^+$ (R = H, CH_3), with one ionised thioamido group, as revealed by an X-ray investigation of [Pt(PPh$_3$)$_2$(*N*HC(*S*)NH$_2$)]$^+$. The preference of *O* versus *S* coordination, as well as the stability of the Pt–O bonds, are discussed in terms of antisymbiosis.

Keywords: Antisymbiosis; Platinum phosphine complexes; Pt–O bonds

1. Introduction

A detailed knowledge of the principles which rule the affinity between metal ions and donor atoms allows the design and synthesis of complexes with particular properties and reactivity, and is useful in fields as different as catalysis, catalysis poisoning, biochemistry and pharmacology [1–9]. For instance, the major drawbacks of cisplatin chemotherapy are toxicity and resistance, both arising, inter alia, from the binding of platinum to sulfur rich proteins [5,6], a cisplatin analogue with low affinity for sulfur would therefore be highly desirable.

The affinity of a metal ion M for a ligand Z is ruled by the hard–soft acid–base (HSAB) principle (sometimes called symbiosis [10]), however if other ligands

* Corresponding authors. Tel.: +39 0250314381; fax: +39 0250314405.
E-mail addresses: mario.manassero@unimi.it (M. Manassero), alessandro.pasini@unimi.it (A. Pasini).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.09.039

are present, in a complex of schematic formula A–M–Z, the nature of the "ancillary" ligand A influences the affinity of M for Z, especially if A and Z are *trans* to each other, and such influence can sometimes reverse the order of affinity dictated by the HSAB principle. This latter behaviour was termed antisymbiosis and was defined as "the preference of a hard donor ligand *trans* to a soft ligand bound to a soft metal centre" [11–14] or "the destabilisation of a soft ligand *trans* to another soft ligand bound to a soft metal centre" [13–18].

In this paper, we wish to describe the results of some studies on Pt(II) phosphine complexes with the hybrid [19,20] ligands L depicted in Scheme 1. These ligands are particularly suitable to study antisymbiosis, because a metal centre can discriminate between two donor sites of different nature, a hard anionic oxygen and a soft neutral sulfur atom. In previous works, we found that when the ancillary ligands are amino groups, the stable species are $[Pt(am)_2(L\text{-}O,S)]^+$ (am = NH_3 or 1/2 ethylenediamine) [21–24], even in the presence of an excess of L^-. On the contrary, in the case of the *cis*-$Pt^{II}(phos)_2$ moiety, not only the chelate complexes $[Pt(L\text{-}O,S)(phos)_2]^+$ can be obtained only with the ligands with the thioether group, sa, sb and sph [24], but also excess of sa^- or sb^- gives the bi-substituted *O*-coordinated $[Pt(L\text{-}O)_2(phos)_2]$ [25] (**a**, **b**). Here, we want to discuss in detail these latter results. Numbering of compounds and abbreviations are reported in Scheme 1.

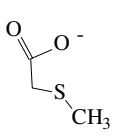
2. Experimental

2.1. General

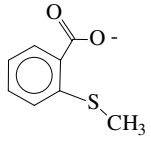
Elemental analyses (C, H, and N) were performed at the Microanalytical Laboratory, the University of Milano. IR (KBr pellets) spectra were recorded on JASCO FT/IR-5300. ^1H and ^{31}P NMR spectra ($CDCl_3$ solutions) were recorded on a Bruker Advance DRX 300. δ values (ppm) are versus external Me_4Si and H_3PO_4, respectively. FAB^+ mass spectra were obtained, from 4-nitrobenzyl alcohol, on a VCA Analytical 7070 EQ, with xenon as the FAB source; isotopic cluster abundance was checked by computer simulation.

All chemicals were of reagent grade. The synthesis of the ligands [21,22], $[Pt(NO_3)_2(phos)_2]$ and $[Pt(L\text{-}O,S)(phos)_2]NO_3$ [24], has been described previously. $[Pt(PPh_3)_3]$ [26] and $[Pt(dppe)_2]$ [27] were obtained following the literature procedures.

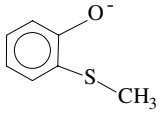
Dihydrogen evolution, during the oxidative addition reactions, was checked by a gas chromatography-mass spectroscopy technique as described in [28].



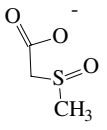
(methylsulfanyl)acetate, sa



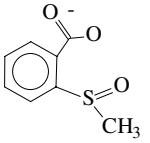
2-(methylsulfanyl)benzoate, sb^-



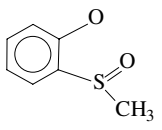
2-(methylsulfanyl)phenolate, sph^-



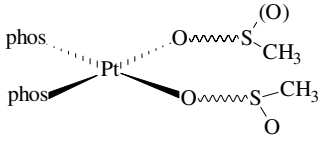
(methylsulfinyl)acetate, soa^-



2-(methylsulfinyl)benzoate, sob^-

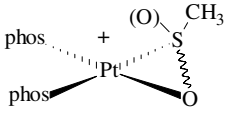


2-(methylsulfiyil)phenolate, $soph^-$



cis-$[Pt(L\text{-}O)_2(phos)_2]$

a (phos = PPh_3; **b** (phos = 1/2 dppe)



$[Pt(L\text{-}O,S)(phos_2]^+$

c (phos = PPh_3); **d** (phos = 1/2 dppe)

Numbering of phosphine compounds												
	$[Pt(L\text{-}O)_2(phos)_2]$						$[Pt(L\text{-}O,S)(phos)_2]^+$					
	L						L					
$(phos)_2$	sa	soa	sb	sob	sph	soph	sa	soa	sb	sob	sph	soph
$(PPh_3)_2$	**1a**	**2a**	**3a**	**4a**	**5a**[§]	**6a**	**1c**	**2c***	**3c**	**4c***	**5c**	**6c**[§]
dppe	**1b**	**2b**	**3b**	**4b**	**5b***	**6b**	**1d**	**2d***	**3d**	**4d**	**5d**	**6d**[§]
* Not obtained. [§] Detected through NMR, but not isolated in the solid state.												

Scheme 1.

2.2. Synthesis of cis-[Pt(L-O)$_2$(phos)$_2$] (**a**–**b** type compounds)

2.2.1. Reaction of [Pt(NO$_3$)$_2$(phos)$_2$] with excess L$^-$: synthesis of bis-(methylsulfinylacetato-O) {bis(diphenylphosphine)ethane}platinum(II) (**2b**)

Potassium methyl-sulfinylacetate was prepared by evaporating to dryness, under reduced pressure, a solution of 0.678 g of Hsoa (0.54 mmol) in 5.3 ml of 0.1 mol L^{-1} aqueous KOH. The residue was treated with 0.136 g (0.21 mmol) of [Pt(dppe)(NO$_3$)$_2$], 10 mL of CH_2Cl_2 and refluxed for 8 h. The filtered solution was concentrated and treated with di-isopropyl ether yielding 0.131 g (74%) of a white precipitate. *Anal.* Calc. for $C_{32}H_{36}O_7P_2PtS_2$:C, 45.0; H, 4.2. Found: C, 44.9, H, 4.1%. IR: 1645, 1338 cm^{-1} (COO); 1028 cm^{-1} (SO). ^{1}H NMR: 2.44 (CH_3S). ^{31}P NMR: 32.4.

The other **a**–**b** compounds were prepared by the same procedure, starting from either *cis*-[Pt(NO$_3$)$_2$(PPh$_3$)$_2$] or [Pt(dppe)(NO$_3$)$_2$]. **5a** was obtained only as a minor component in the reaction mixture and could not be isolated. Reaction of *cis*-[Pt(dppe)(NO$_3$)$_2$] with excess Ksph gave only **5d**. Analyses and spectral data are reported in the supplementary material.

2.2.2. Reaction of the chelate [Pt(L-S,O)(PPh$_3$)$_2$]NO$_3$ with L$^-$: synthesis of cis-bis(methylsulfanylacetato-O)-bis(triphenylphosphine)platinum(II) (**1a**)

Potassium methylsulfanylacetate was prepared as above from 3.4 mL of aqueous 0.1 mol L^{-1} KOH and 0.036 g (0.34 mmol) of methylsulfanylacetic acid. An equimolar amount of [Pt(PPh$_3$)$_2$(sa-*O*,*S*)]NO$_3$ (0.300 g dissolved in in 40 mL of CH_2Cl_2) was added to the residue. The slurry was refluxed for 8 h, filtered and concentrated to 3 mL under reduced pressure. The white product was obtained by addition of di-isopropyl ether. Yield: 88%, 0.278 g. *Anal.* Calc. for $C_{42}H_{40}O_4P_2PtS_2$: C, 54.2; H, 4.3. Found: C, 54.0; H, 4.1%. IR: 1637, 1330 cm^{-1} (COO). ^{1}H NMR: 1.89 (CH_3S). ^{31}P NMR: 6.54 (J_{PtP}, 3817 Hz).

Compounds **3a**, **1b** and **3b** were obtained in the same way in 80–90% yields.

2.2.3. Oxidative addition reactions of HL to [Pt(PPh$_3$)$_3$]: alternative synthesis of compounds **a**. cis-bis(methylsulfanylacetato-O)bis(triphenylphosphine)platinum(II) (**1a**)

A solution of 0.051 g of methylsulfanylacetic acid (0.48 mmol) in 5 mL of CH_2Cl_2 was added to a cold (ice bath) solution of 0.235 g of [Pt(PPh$_3$)$_3$] (0.24 mmol) in 20 mL of CH_2Cl_2, under a nitrogen atmosphere. The yellow colour faded within a few minutes and the colourless solution was kept in the cold for two hours, concentrated under reduced pressure, and 0.206 g (92%) of the white product was obtained by the addition of di-isopropyl ether.

The same procedure was employed for **2a, 3a, 4a** and **6a**, which were obtained in 80–90% yields. In the case of the reaction with Hsph, compound **5a** was identified as a minor component of the reaction mixture by ^{31}P NMR, together with **5c**.

2.3. Reactivity

2.3.1. Reaction of the phosphine complexes with pyridine: [(methylsulfanyl)benzoato-O]bis-(triphenylphosphine)-(pyridine)platinum(II) nitrate, **7a**(NO$_3$)

A CH_2Cl_2 solution (20 mL) of equimolar amounts of pyridine (0.006 g) and [Pt(PPh$_3$)$_2$(sb-*O*,*S*)[NO$_3$ (0.071 g, 0.076 mmol) was heated at 30 °C for 2 h. The product was obtained as a CH_2Cl_2 solvate by concentration and addition of di-isopropyl ether. Yield: 84% (0.065 g). *Anal.* Calc. for $C_{49.25}H_{42.5}Cl_{0.5}N_2O_5P_2PtS$ (**7a**(NO$_3$).1/4 CH_2Cl_2): C, 56.3; H, 4.6; N, 2.5. Found: C, 56.4; H, 4.4; N, 2.7%. IR: 1623, 1334 cm^{-1} (COO). ^{1}H NMR: 2.18 (CH_3S); 8.73 (J_{Pt-H}, 30–9 Hz, α hydrogen of py). ^{31}P NMR: 5.10, (d, J_{PP} 21.2Hz; J_{Ptp}, 3391 Hz, *trans* to N); 7.59 (d; J_{PtP}, 3688 Hz, *trans* to O).

Reaction of 0.060 g (0.072 mmol) [Pt(dppe)(sb-*O*,*S*)]NO$_3$ with 0.006 g of pyridine gave 0.054 g (83%) of bis-[(diphenylphosphine)ethane](methyl sulfanylbenzoato)(pyridine)platinum(II) nitrate, **7b**(NO$_3$). *Anal.* Calc. for $C_{39}H_{36}N_2O_5P_2PtS$: C, 51.8; H, 4.3; N, 3.3. Found: C, 51.9; H, 4.1; N, 3.2%. IR: 1625, 1338 cm^{-1} (COO). ^{1}H NMR: 2.21 (CH_3S); 8.43 (J_{Ptp}, 29.0 Hz). ^{31}P NMR: 35.07 (d, J_{PP}, 7.0 Hz; J_{PtP}, 3519 Hz, *trans* to O), 35.43 (d; J_{PtP}, 3406, *trans* to N).

Complexes **a** and **b**, as well as the other **c**–**d**, failed to react under the same conditions.

2.3.2. Reactions of the phosphine complexes with dimethylsulfoxide

These reactions were carried out by dissolving 1 mL of Me_2SO and 0.08 mmol of either **a**–**b** or **c**–**d** complexes in 15 mL of CH_2Cl_2 and boiling the solution for 8 h. In all cases, concentration and addition of di-isopropyl ether gave the unreacted starting material.

2.3.3. Reactions of **a**–**d** complexes with sodium diethyldithiocarbamate

These reactions were performed by treating, at room temperature, ethanol solutions of complexes **a**–**d** with a slight excess of Na(Et$_2$NCS$_2$) · 3H$_2$O. After 2 h, addition of di-isopropyl ether gave the L$^-$ salts of **8a**, or **8b** as oily products which were used as such for spectral characterisation. Analytically pure samples were obtained in 80–90% yield by the addition of a water solution of Na(BF$_4$) to ethanol solutions of the products.

[Pt(Et$_2$NCS$_2$)(PPh$_3$)$_2$](BF$_4$), **8a**(BF$_4$): FAB$^+$: *m*/*z* 867. (calc. for [Pt(Et$_2$NCS$_2$)(PPh$_3$)$_2$]$^+$, 867).

[Pt(dppe)(Et_2NCS_2)](BF_4), **8b**$_4$(BF_4): FAB^+, *m/z*, 741 (calc. for [Pt(dppe)(Et_2NCS_2)]$^+$, 741). Analyses and spectral data are reported in the supplementary material.

2.3.4. Reaction of **a**–**d** complexes with thiourea or *N,N′*-dimethylthiourea

bis-(triphenylphosphine)[thioureato-(N,S)} platinum(II) tetrafuroborate, **9a**(BF_4).

An ethanol solution (15 mL) of 0.070 g (0.066 mmol) of [Pt(PPh_3)$_2$(sb-*O*)$_2$] and 0.050 g of thiourea was stirred at room temperature for one hour. Concentration to drops and addition of di-isopropyl ether gave a white product, which was crystallised as the BF_4 salt by the addition of 0.011 g of $NaBF_4$ in 15 mL of water. Yield: 88%, 0.051 g. *Anal.* Calc. for $C_{37}H_{33}BF_4N_2P_2PtS$: C, 50.4; H, 3.8; N, 3.2%. Found: C, 50.5; H, 3.9; N, 3.4. ^{31}P NMR: 11.55 (d, J_{PP}, 20.0 Hz; J_{PtP}, 3360 Hz), 14.70 (d; J_{PtP}, 3240 Hz). FAB^+: *m/z*, 794 (calc. for [Pt(NHSCNH$_2$)(PPh_3)$_2$]$^+$ 794).

The same procedure was used for all **a**–**d** complexes. The dppe **d** derivatives gave decomposition products, with the exception of bis-{(diphenylphosphine)ethane}{thioureato-(N,S)}platinum(II), which precipitated spontaneously from the reaction mixture as the sb salt. **9b**(sb) in 60% yield. *Anal.* Calc for $C_{35}H_{34}N_2O_2P_2PtS_2$: C, 50.3; H, 4.1; N, 3.4. Found: C, 50.5; H, 4.0; N, 3.4%. ^{31}P NMR: 38.33 (d, J_{PP}, 7.2 Hz; J_{PtP}, 3220 Hz); 41.37 (d, J_{PtP}, 3203 Hz). FAB^+: *m/z* 668 (calc. for [Pt(dppe)(NHCSNH$_2$)]$^+$, 668.

The reactions with *N,N′*-dimethylthiourea were performed in a similar way. **10a**(BF_4): *Anal.* Calc for $C_{39}H_{37}BF_4N_2P_2PtS$: C, 51.5; H, 4.1; N, 3.1. Found: 51.4; H, 4.2; N, 3.0%. ^{1}H NMR: 2.16 (d, J_{P-H}, 3.9 Hz; J_{Pt-H}, 30.7 Hz; CH_3N^-); 2.78 (d, J_{H-H}, 4.39 Hz; CH_3NH); 8.15 (d, J_{H-H}, 4.39 Hz; NH). ^{31}P NMR: 12.11 (d, J_{P-P}, 22.9 Hz; J_{Pt-P}, 3319 Hz); 16.85 (d; J_{Pt-P}, 3220 Hz).

10b(NO_3). *Anal.* Calc for $C_{29}H_{31}N_3O_3P_2PtS$: C, 45.9; H, 4.1; N, 5.5. Found: C, 45.6; H, 4.4; N, 5.4%. ^{1}H NMR: 2.65 (d, J_{P-H}, 4.1 Hz; J_{Pt-H}, 37.2 Hz; CH_3N^-); 2.92 (br, CH_3NH); 8.25 (br, NH). ^{31}P NMR: 37.42 (d, J_{P-P}, 7.5 Hz; J_{PtP}, 3105 Hz); 45.05 (d; J_{PtP}, 3235 Hz).

2.3.5. Reaction of complexes **a**–**d** with tetramethylthiourea

Solutions of the complexes (typically 0.1 mmol in 30 mL of CH_2Cl_2) and an excess of tetramethylthiourea (tmtu) were left at room temperature for 2–6 h. Complexes **a**–**b** were recovered unreacted; **1c**, **1d**, **5c** and **5d** reacted slowly, with some decomposition, while **3c** and **3d** gave analytically pure *cis*-[Pt(PPh_3)$_2$(sb-*O*)(tmtu)](NO_3), **11a** and [Pt(dppe)(sb-*O*)(tmtu)](NO_3), **11b**, respectively, by the addition of di-isopropyl ether to the concentrated solutions.

11a(NO_3) · H_2O. *Anal.* Calc. for $C_{49}H_{51}N_3O_6P_2PtS_2$: C, 53.5; H, 4.7; N, 3.8. Found: C, 53.4; H, 4.6; N, 4.1%. ^{1}H NMR: 2.32 (CH_3S of sb); 3.01 (CH_3 of tmtu). ^{31}P NMR: 5.53 (d, J_{P-P}, 19.0 Hz; J_{PtP}, 3624, *trans* to O); 18.78 (d; J_{PtP}, 3258 Hz, *trans* to S). FAB^+ MS: 1019 (calc. 1019).

11b(NO_3) · H_2O. *Anal.* Calc. for $C_{39}H_{39}N_3O_6P_2PtS_2$: C, 48.4; H, 4.0; N, 4.4. Found: C, 48.7; H, 4.2; N, 4.6%. ^{1}H NMR: 2.30 (CH_3S of sb); 2.96 (CH_3 of tmtu). ^{31}P NMR: 34.23 (d, J_{P-P}, 6.0 Hz; J_{PtP}, 3530Hz, *trans* to O); 48.41 (d; J_{PtP}, 3041, *trans* to S).

2.3.6. Reactions of the *[Pt(en)(L-O,S)]*$^+$ complexes with sodium diethyldithiocarbamate

The reaction of equimolar amounts of [Pt(en)(sa-*O,S*)]NO_3 [22] and Na(dttc) · $3H_2O$ (0.096 g and 51.5 g, respectively, 0.227 mmol) was performed in 20 mL of water, at room temperature. The readily formed yellow solid was filtered off and was found to be [Pt(dttc)$_2$] by comparison with an authentic sample. All [Pt(en)(L-*O,S*)]NO_3 complexes behaved in a similar way.

2.3.7. Reaction of *[Pt(en)(sa-O,S)]NO*$_3$ with thiourea: synthesis of (ethylenediamine) {methylsulfanyl-acetato-(S)}(thiourea)platinum(II) nitrate hydrate, *[Pt(en)-(sa-S)(tu)]NO*$_3$ · *H*$_2$*O*

This compound was obtained by mixing 0.111 g (0.263 mmol) of [Pt(en)(sa-*O,S*)]NO_3 with an equimolar amount of thiourea (0–020 g) in 20 mL of water. After 4 h at room temperature the solution was concentrated to 2 mL under reduced pressure, addition of ethanol (6 mL) and di-isopropyl ether (15 mL) gave 0.046 g (35%) of a white solid. *Anal.* Calc. for $C_6H_{19}N_5O_6PtS_2$: C, 13.9; H, 3.7; N, 13.6. Found: C, 13.7; H, 3.7; N, 13.9%. IR: 1595 cm^{-1} (ν_{asym} uncoordinated CO_2^-), 1384 cm^{-1} (ionic NO_3^-). ^{1}H NMR: 2.45 (s, J_{Pt-H} 44.8 Hz, CH_3S); 3.60 (b, J_{Pt-H} about 51 Hz, CH_2S); 2.7 (mt,b, J_{Pt-H} about 40 Hz).

2.3.8. (Ethylenediamine)bis(thiourea)platinum(II) nitrate methylsulfanylacetate, *[Pt(en)(tu)*$_2$*]NO*$_3$ *sa*

Reaction of [Pt(en)(sa-*S*)(tu)] (0.016 g, 0.034 mmol) with 0.003 g (0.016 mmol) of thiourea in 10 mL of water gave, after 3 h, and concentration under reduced pressure, [Pt(en)(tu)$_2$](NO_3)(sa), which was characterised by spectroscopy. IR, 1560 cm^{-1} (free CO_2^- of sa), 1384 cm^{-1} (ionic NO_3). ^{1}H MNR: δ, 2.06 (s, CH_3S of free sa$^-$); 3.12 (s, CH_2 of sa$^-$); 2.84 (b, J_{Pt-H} 40.7 Hz, CH_2 of en).

2.4. X-ray data collections and structure determinations

Crystal data are summarised in Table 1; other experimental details are listed in the supporting information. The diffraction experiments were carried out on a Bruker SMART CCD area-detector diffractometer at room temperature. Crystals of **9a**(NO_3) gave a good diffrac-

Table 1
Crystallographic data

Compound	**3a** · H_2O	**9a**NO_3
Formula	$C_{52}H_{46}O_5P_2PtS_2$	$C_{37}H_{33}N_3O_3P_2PtS$
M	1072.11	856.80
Color	colourless	colourless
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	19.708 (2)	12.969 (1)
b (Å)	11.792 (1)	23.550 (2)
c (Å)	21.733 (2)	13.019 (1)
α (°)	90	90
β (°)	93.73 (1)	118.66 (1)
γ (°)	90	90
U (Å^3)	5040.0 (9)	3489.1 (4)
Z	4	4
F(000)	2152	1696
D_c (g cm^{-3})	1.413	1.631
T (K)	293	293
Crystal dimensions (mm)	0.141 × 0.215 × 0.519	0.141 × 0.338 × 0.423
μ(Mo Kα) (cm^{-1})	30.0	42.5
Min. and max. transmiss. Factors	0.476–1.00	0.416–1.00
Scan mode	ω	ω
Frame width (°)	0.30	0.30
Time per frame (s)	15	25
No. of frames	2450	2450
Detector-sample distance (cm)	4.00	4.00
θ-Range	3–23	3–27
Reciprocal space explored	full sphere	full sphere
No. of reflections (total; independent)	48195, 7274	57643, 10646
R_{int}	0.0925	0.0362
Final R_2 and R_{2w} indices[a] (*F2*, all reflections)	0.115, 0.126	0.056, 0.073
Conventional R_1 index [$I > 2\sigma(I)$]	0.053	0.029
Reflections with $I > 2\sigma(I)$	4487	7975
No. of variables	559	433
Goodness of fit[b]	1.25	1.04

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w/(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.
[b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and *p*, the ignorance factor, = 0.04 for both **3a** · H_2O and **9a**NO_3.

tion, whereas crystals of **3a** · H_2O gave a diffraction of poor quality and within a θ range limited to 21°. No crystal decay was observed, hence no time-decay correction was needed. The collected frames were processed with the software SAINT [29] and an empirical absorption correction was applied (SADABS) [30] to the collected reflections. The calculations were performed using the Personal Structure Determination Package [31] and the physical constants tabulated therein [32]. The structures were solved by direct methods (SHELXS) [33] and refined by full-matrix least-squares using all reflections and minimising the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). Anisotropic thermal factors were refined for all the non-hydrogen atoms. The three hydrogen atoms bonded to N(1) and N(2) in **9a**(NO_3) were refined with fixed isotropic thermal factors. The hydrogen atoms of the water molecule in **3a** · H_2O were neglected. The remaining hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter *B* 1.10 times that of the carbon atom to which they are attached, and not refined. In the final Fourier maps, the maximum residuals were 3.44(45) e Å^{-3} at 1.05 Åfrom Pt and 2.34(21) e Å^{-3} at 0.89 Åfrom Pt for **3a** · H_2O and **9a**NO_3, respectively. CCDC nos. 231102 and 231103 contain the supplementary crystallographic data for this paper.

3. Results and discussion

3.1. Syntheses of *a* and *b* type compounds

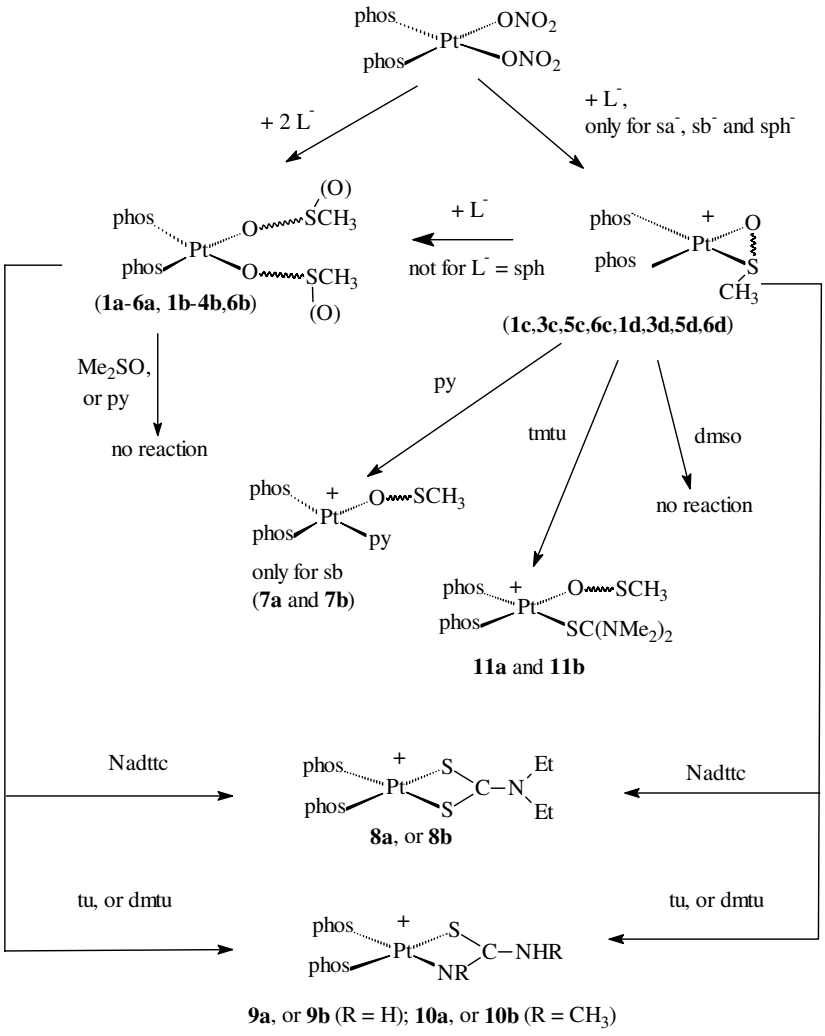
These compounds were obtained by the following reactions, whose outcome shows also the preference of the $Pt(phos)_2^{2+}$ fragment for O, rather than S donor atoms (see Scheme 2):

1. Substitution of labile ligands of Pt-phosphine complexes
   cis-$[Pt(NO_3)_2(phos)_2]$ + 2 KL
   → $[Pt(L\text{-}O)_2(phos)_2]$ + 2 KNO_3
2. Reaction of excess L^- with the chelate **c**–**d** complexes
   $[Pt(L\text{-}O,S)(phos)_2]^+ + KL \rightarrow [Pt(L\text{-}O)_2(phos)_2] + K^+$
   only the sa, sb and sph **c**–**d** derivatives are available [24,25].
3. An alternative route to compound **a** is the oxidative addition of HL to a Pt(0) derivative
   $[Pt(PPh_3)_3] + 2 \quad HL \rightarrow cis\text{-}[Pt(L\text{-}O)_2(phos)_2] + H_2$
   Formation of dihydrogen, confirmed by gas mass spectroscopy [28], suggests an intermediate hydrido-Pt^{II} species, which upon reaction with a second mole of HL yields the product and H_2. We were unable to detect such intermediate.

All ligands L gave the bi-substituted *O*-coordinated compounds $[Pt(L\text{-}O)_2(phos)_2]$; **5a** was obtained only in traces, **5b** was not obtained.

3.2. Spectroscopic evidence for O-coordination of L in *a* and *b* compounds

Infrared spectra. The carboxylato stretching frequencies of compounds **1a**–**4a** and **1b**–**4b** are as expected for unidentate carboxylato groups [34]. Stretching frequencies of the sulfoxide groups in **2a**, **4a**, **2b** and **4b**



Scheme 2.

are similar to those of the free anions L^-, showing that these groups are not involved in coordination.

In ^1H NMR spectra, the δ values of the SCH_3 protons are similar to those of free L^- and show neither P–H nor Pt–H coupling, which instead we always observed in the case of *S*-coordination of these ligands to Pt^{II} [21–24].

Phosphorus-31 NMR spectra display one singlet, with Pt satellites, showing equivalence of the two P atoms. Pt–P coupling constants of **1**–**4**, **a**–**b** are around 3600–3800 Hz, close to the values reported for *cis*-$[Pt(PPh_3)_2(RCOO\text{-}O)_2]$ [35] and [Pt(dppe)(malonato-*O,O*')] [36]. J_{Pt-P} of the phenolato complexes **5** and **6**, are lower, as observed in similar cases [24,37,38]: alkoxo groups are strong σ donors which compete more effectively with a *trans* phosphine [38]. The Pt–P coupling constants in (neutral) compounds **a** and **b** are higher than those of P *trans* to the carboxylato groups in (cationic) **c** and **d**, presumably because the negatively charged L's are more tightly bound to Pt in the latter, with consequent lowering of the Pt–P bond strength. Compare literature data: J_{Pt-P} *trans* to carboxylato are 3700–3800 Hz in [Pt(dppe)(malonato-*O,O*')] [36] and 3400–3500 Hz in [Pt(dppe)(phosphine)(carboxylato-*O*)]$^+$ [39].

3.3. Structure of $[Pt(PPh_3)_2(sb\text{-}O)_2]$. H_2O $(3a \cdot H_2O)$

O-coordination was confirmed for **3a** by an X-ray structure determination. Crystals of the monohydrate were obtained by slow diffusion of cyclohexane into a CH_2Cl_2 solution. Although the crystals were of poor quality (see Section 2), we report this structure as a final proof of *O*-coordination of L's in these complexes. An ORTEP [40] view of the complex is shown in Fig. 1, whose caption reports relevant bond lengths and angles. The metal is four coordinate with two *cis*-triphenylphosphine and two *cis*, *O*-coordinated sb anions.

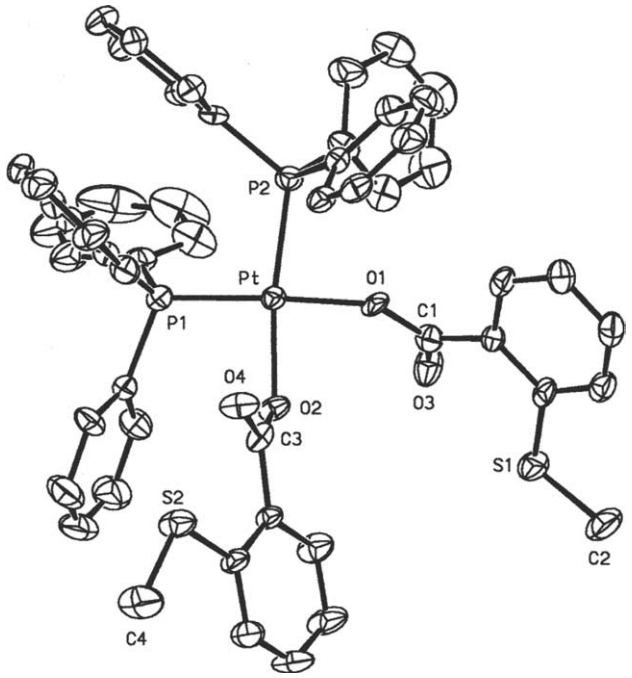


Fig. 1. ORTEP view of $[Pt(PPh_3)_2(sb\text{-}O)_2]$. H_2O (**3a** · H_2O). Selected bond distances (Å) and angles (°): Pt–P(1), 2.227(3); Pt–P(2), 2.269(3); Pt–O(1), 2.049(6); Pt–O(2), 2.080(6). P(1)–Pt–P(2), 98.1(1); P(1)–Pt–O(1), 173.9(2); P(1)–Pt–O(2), 90.6(2); P(2)–Pt–O(1), 85.3(2); P(2)–Pt–O(2), 171.2(2); O(1)–PtO(2), 85.9(2).

3.4. Stability and reactivity studies

Having observed the preference of the *cis*-$Pt^{II}(phos)_2$ moieties for O rather than S donor atoms, shown by the above results, we wanted to look at the stability of such Pt–O bonds in the presence of other ligands, by performing the reactions summarised in Scheme 2.

Compounds **a**–**b** are recovered unreacted in the presence of either Me_2SO or pyridine. As for **c**–**d**, only **3c** and **3d** reacted, and only with pyridine, yielding $[Pt(L\text{-}O)(phos)_2(py)]^+$ (**7a** and **7b**).

Substitution of the Pt–O bonds was achieved only with reagents capable of forming stable chelate rings with Pt(II). Thus, *N*,*N*′ diethyldithiocarbamate ($dttc^-$) reacts with all compounds **a**–**d** yielding the known [41,42] $[Pt(dttc)(phos)_2]^+$, **8a** and **8b**. Moreover, also thiourea (tu) and *N*,*N*′-dimethylthiourea react with compounds **a**–**d** forming the cyclometallated derivatives $[Pt(phos)_2(NRCSNHR)]^+$ (R = H, **9a** and **9b** or R = CH_3, **10a** and **10b**), with a deprotonated thioamido group, characterised by comparison of spectral data with those of similar complexes [43–45]. Tetramethylthiourea (tmtu), which does not form cyclometallation under these conditions, reacts only with **3c** and **3d** giving $[Pt(phos)_2(sb\text{-}O)(tmtu)]^+$, **11a** and **11b**, again with retention in the Pt–O bonds.

3.5. Structure of $[Pt(NHCSNH_2)(PPh_3)_2]NO_3$, **9a**$(NO_3)$

A proof for cyclometallation of thiourea was obtained by the X-ray structure determination of **9a**. To our knowledge, the only reported structures of cyclometallated thioureato Pt–phosphine complexes [44,45] are all derivatives of *N*-substituted thiourea $RNHCSNR^-$ and not of unsubstituted thiourea NH_2CSNH^-.

Crystals were obtained by cyclohexane diffusion into a $CHCl_3$ solution of the product of the reaction of **3c**(NO_3) with tu. The structure consists of the packing of **9a** cations and NO_3^- anions in a 1:1 molar ratio. An ORTEP view of the cationic complex is shown in Fig. 2, selected bond distances and angles are reported in the Figure caption. Two *cis* phosphines, the sulfur atom and the NH^- group of tu, complete the coordination set, which is planar with a slight square pyramidal distortion, maximum distances from the best plane being +0.066(1) Åfor Pt and −0.076(3) for S. The Pt–P(1) bond (*trans* to S) is longer than Pt–P(2) and, is in a range normal for PPh_3 *trans* to S (thiourea) [44–46]. The Pt–S and Pt–N bond distances are also comparable to those of N-substituted thioureato complexes, showing that substitution at the N position of thiourea does not affect the bonding ability of the deprotonated thioamido group in an appreciable way.

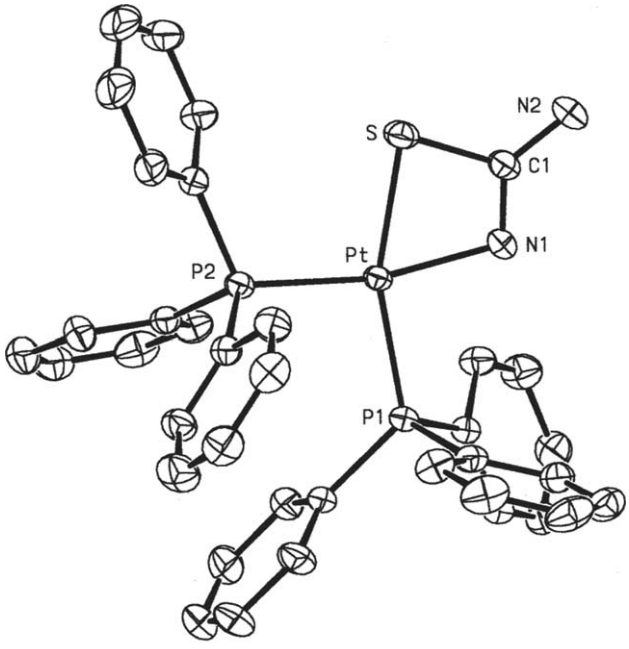
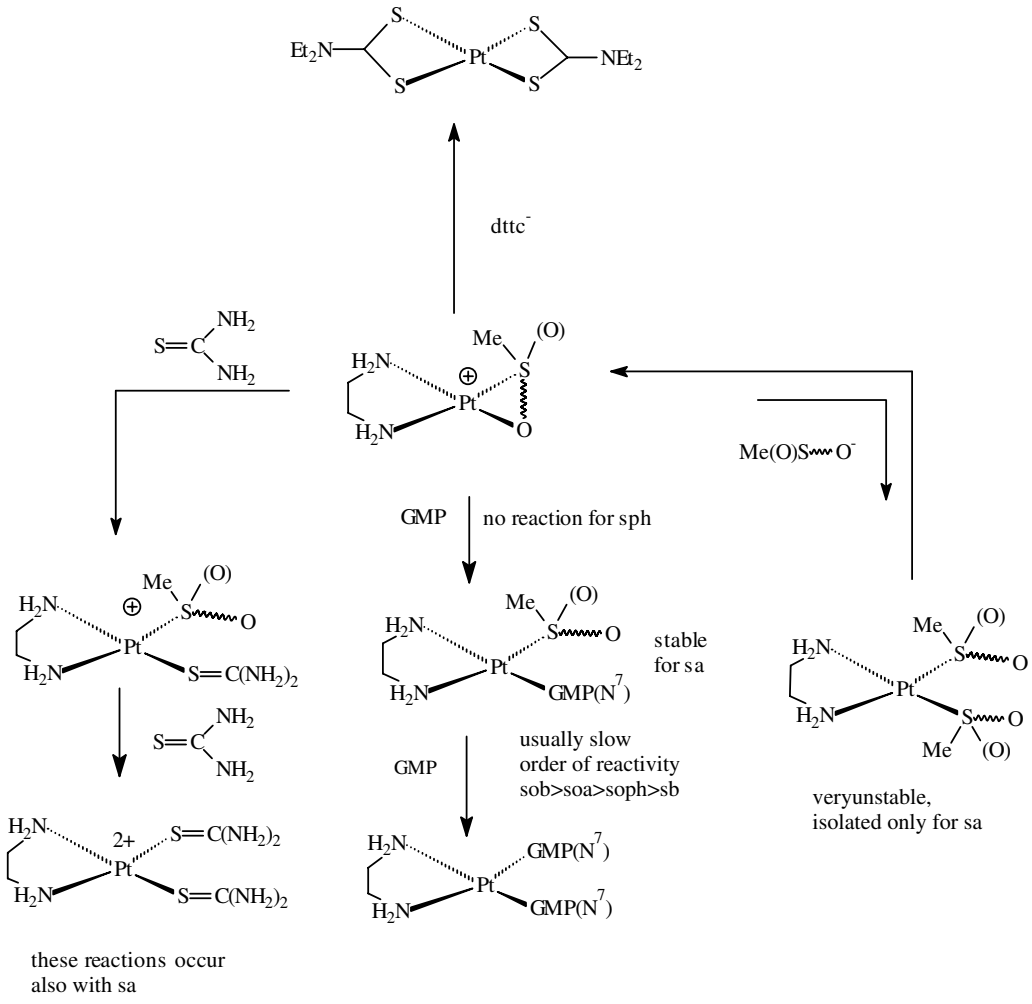


Fig. 2. ORTEP view of **9a**(NO_3). Selected bond distances (Å) and angles (°): Pt–S, 2.363(1); Pt–P, 2.291(1); Pt–P(2), 2.251(1); Pt–N(1), 2.058(2). S–Pt-P(1), 160.40(2); S–Pt–P(2), 97.86(3); S–Pt–N(1), 68.94; P(1)–Pt–P(2), 100.37(3); P(1)–Pt–N(1), 92.66(8); P(2)–Pt–N(1), 166.79(8).



Scheme 3.

3.6. Comparison with the reactivity of $[Pt(en)_2(L\text{-}O,S)]^+$

The reactivity of these complexes [21–24] is summarised in Scheme 3, which reports also the reactions with $dttc^-$ and thiourea, performed for comparison purposes. The $[Pt(L\text{-}O,S)(NH_3)_2]^+$ derivatives are not included, since they easily lose the amino ligands [24] and are therefore unsuitable for comparison.

A first difference with the phosphine complexes is that upon reaction with nucleophiles (Nu), like GMP, tu, as well as an excess of L^-, chelate ring opening of L occurs at the Pt–O bond, with formation of [Pt(en)(L-*S*)(Nu)]. In these species, the Pt–S bonds are little reactive, thus, for instance, cyclometallation of tu does not occur. A second difference is the high stability of the chelate ring of L's in the en complexes: the bi-substituted species $[Pt(en)(L\text{-}S)_2]$ can be observed in solution, but are little stable, they lose one L giving the chelate $[Pt(en)(L\text{-}O,S)]^+$ [23]. On the contrary, in the phosphine complexes, the stability of the chelate ring is overcome by the preference for *O*-coordination.

4. Conclusions

By using the ligands presented here, we have shown that if the $Pt^{II}(phos)_2$ fragment has the possibility of choosing between *O* and *S* coordination, the former is preferred. The Pt–O bonds thus formed are reluctant to substitution, since they react only with reagents which form very stable chelate rings with Pt^{II}.

Among the factors which can contribute to the preference of such a *cis*-PtO_2P_2 coordination set, one can envisage steric requirements: *O*-coordination of L's is less sterically demanding than *S*-coordination, a factor that is more important with phenylphosphine than with en complexes. Steric hindrance has indeed been proposed [17] to be the origin of *O*-coordination of Me_2SO in *cis*-$[Pt(Me_2SO\text{-}O)_2(PPh_3)_2]^{2+}$, but in the case of the less sterically demanding $[Pt(Me_2SO)_2(PMe_3)_2]$ the re-

ported J_{Pt-P} values [47] strongly suggest *O*-coordination of Me_2SO. We therefore believe that a major role for the preference for *O*-coordination here described must be attributed to antisymbiosis.

As pointed out in the introduction, antisymbiosis is defined as the preference of a hard donor ligand *trans* to a soft ligand attached to a soft metal ion [13]. This effect is strictly related to the orbitals utilised to form the metal-ligand bonds. Ligands in *trans* to each other compete for the same orbitals for both σ and π bonds, therefore, because of the π component of the Pt–phosphine bond, it is advantageous to have a hard ligand, with only σ Pt–L component, *trans* to P [14].

Antisymbiosis has relevant effects in coordination chemistry: it explains the difficulty of obtaining certain isomers in square planar complexes [48], some cases of linkage isomerism [11,13,47–50], as in $[Pt(Me_2SO\text{-}O)_2(Me_2SO\text{-}S)_2]^{2+}$ [51], as well as the outcome of certain reactions; for instance, we may cite the remarkable reactivity reported for *cis*-$[Pt(acO\text{-}O)_2(Et_2S)_2]$, which, upon treatment with quinones, gives $[Pt(Et_2S)_2(quinone\text{-}O,O')]$, while reaction with PPh_3 yields *cis*-$[Pt(acO\text{-}O)_2(PPh_3)_2]$ [52].

The ligands of Scheme 1 are suitable for studying this effect. More work is being planned to investigate this effect in more details.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 231102 (**3a** · H_2O) and 231103 (**9a**(NO_3)). Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

A file containing elemental analyses, Ir, ^1H and ^{31}P NMR spectra of all compounds can be obtained by the author (A.P.) on request at his e-mail address.

Acknowledgements

We thank Prof. A. Recchia, the University of Insubria, for the mass spectrometry analysis of dihydrogen evolution. This work has been financed by the Ministero per l'Istruzione e la Ricerca (MIUR).

References

[1] A. Shaver, M. El-khateeb, A.-M. Lebuis, Inorg. Chem. 40 (2001) 5288.
[2] J.C. Bayon, C. Claver, A.M. Masdeu-Bultò, Coord. Chem. Rev. 193–195 (1999) 73.
[3] A. Iretskii, H. Adams, J.J. Garcia, G. Picazo, P.M. Maitlis, Chem. Commun. (1998) 61.
[4] C. Bianchini, A. Meli, Acc. Chem. Res. 31 (1998) 109.
[5] V. Brabec, J. Kasparkova, Drug Resist. Updates 5 (2002) 147.
[6] J. Reedijk, Chem. Rev. 99 (1999) 2499.
[7] K.J. Narnham, M. I Djuran, D.d.S. Murdoch, P.J. Sadler, Chem. Commun. (1994) 721.
[8] A. Paolicchi, E. Lorenzini, P. Perego, R. Supino, F. Zunino, M. Comporti, A. Pompella, Int. J. Cancer (2002) 740.
[9] T. Pelleg-Schulman, D. Gibson, J. Am. Chem. Soc. 123 (2001) 3171.
[10] C.K. Jorgensen, Inorg. Chem. 3 (1964) 1201.
[11] N.J. De Stefano, J.L. Burmeister, Inorg. Chem. 10 (1971) 998.
[12] For instance J. Chatt, B.T. Heaton, J. Chem. Soc. A (1968) 2745.
[13] R.G. Pearson, Inorg. Chem. 12 (1973) 712.
[14] R.G. Pearson, Chemical Hardness, Wiley VCH, Weinheim, 1997, p. 15.
[15] R. Navarro, E. Urriolabeita, J. Chem. Soc., Dalton Trans. (1999) 4111.
[16] J.N. Harvey, K.M. Heslop, A.G. Orpen, P.G. Pringle, Chem. Commun. (2003) 278.
[17] F.R. Hartley, S.G. Murray, A. Wilkinson, Inorg. Chem. 28 (1989) 549.
[18] J.A. Davies, F.R. Hartley, Chem. Rev. 81 (1981) 79.
[19] P.B. Braunstein, F. Naud, Angew. Chem. 113 (2001) 702.
[20] P.B. Braunstein, F. Naud, Angew. Chem., In. Ed. 40 (2001) 682.
[21] A. Pasini, G. D'alfonso, C. Manzotti, M. Moret, S. Spinelli, M. Valsecchi, Inorg. Chem. 33 (1994) 4140.
[22] A. Pasini, P. Perego, M. Balconi, M. Lupatini, J. Chem. Soc., Dalton Trans. (1995) 579.
[23] A. Pasini, M. Moroni, J. Chem. Soc., Dalton Trans. (1997) 1093.
[24] A. Pasini, S. Rizzato, D. De Cillis, Inorg. Chim. Acta 315 (2001) 196.
[25] L. Battan, M. Manassero, A. Pasini, Inorg. Chem. Commun. 4 (2001) 606.
[26] R. Ugo, F. Cariati, G. La Monica, Inorg. Synth. 11 (1968) 105.
[27] K.R. Laing, S.D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton Trans. (1974) 1205.
[28] C. Dossi, A. Fusi, R. Psaro, Thermochim. Acta 236 (1994) 165.
[29] SAINT Reference Manual, Siemens Energy and Automation, Madison, W1, 1994–1996.
[30] G.M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Gottingen, 1997.
[31] B.A. Frenz, Comput. Phys. 2 (1988) 42.
[32] Crystallographic Computing 5, Oxford University Press, Oxford, UK, 1991, Chapter 11, p. 126.
[33] G.M. Sheldrick, SHELXS 86. Program for the solution of crystal structures, 1985.
[34] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
[35] A.L. Tan, P.M.N. Low, Z.-Y. Zhou, W. Zheng, B.-M. Wu, T.C.W. Mak, T.S.A. Hor, J. Chem. Soc., Dalton Trans. (1996) 2207.
[36] A.R. Khokhar, Q. Xu, Z.H. Siddik, J. Inorg. Biochem. 39 (1990) 117.
[37] H. Yuge, T.K. Miyamoto, Inorg. Chim. Acta 279 (1998) 105.
[38] N.W. Alcock, A.W.G. Platt, P. Pringle, J. Chem. Soc., Dalton Trans. (1987) 2273.
[39] G.K. Anderson, G.J. Lumetta, Inorg. Chim. Acta 118 (1986) L9.
[40] C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
[41] R. Colton, T.A. Stephenson, Polyhedron 3 (1984) 231.
[42] G. Exarchos, S.D. Robinson, J.W. Steed, Polyhedron 20 (2001) 2951.
[43] P.L. Watson, J.A. Albanese, J.C. Calabrese, D.W. Ovenall, R.G. Smith, Inorg. Chem. 30 (1991) 4638.
[44] W. Henderson, B.K. Nicholson, C.E.F. Rickard, Inorg. Chim. Acta 320 (2001) 101.
[45] S. Okeya, Y. Fujiwara, S. Kawashima, Y. Hayashi, K. Isobe, Y. Nakamura, H. Shimimura, Y. Kushi, Chem. Lett. (1992) 1823.

[46] S. Fantasia, M. Manassero, A. Pasini, Inorg. Chem. Commun. 7 (2004) 97.
[47] G. Trovò, B. Longato, B. Corain, A. Tapparo, A. Furlani, V. Scarcia, F. Baccichetti, F. Bordin, M. Palumbo, J. Chem. Soc., Dalton Trans. (1993) 1547.
[48] L.I. Elding, A. Oskarsson, Inorg. Chim. Acta 130 (1987) 209.
[49] N.N. Akhtar, A.A. Isab, A.R. Al-Arfaj, M.S. Hussein, Polyhedron 16 (1997) 125.
[50] J.B. Melpolder, J.L. Burmeister, Inorg. Chim. Acta 49 (1981) 115.
[51] J. Vicente, A. Arcas, D. Bautista, P.G. Jones, Organometallics 16 (1997) 2127.
[52] J. Kuyper, Inorg. Chem. 18 (1979) 1484.