Nickel dithiolene complexes as a source of a new family of S,S-dinegative chiral ligands R₄btimdt = 5,5′-bis(1,3-dialkyl-4-imidazolidine-2-thione-4-thiolate)

Francesco Bigoli,[a] **Simona Curreli,**[b] **Paola Deplano,**[*b] **Laura Leoni,**[b] **Maria Laura Mercuri,**[b] **Maria Angela Pellinghelli,**[a] **Angela Serpe**[b] **and Emanuele F. Trogu**[b]

[a] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Viale delle Scienze 78, I-43100 Parma, Italy*

[b] *Dipartimento di Chimica Inorganica ed Analitica, Università di Cagliari, Cittadella di Monserrato, I-09042 Monserrato, Cagliari, Italy. E-mail: deplano@vaxca1.unica.it*

The reaction of the complex [Ni(Bu₂timdt)₂] (Bu₂timdt = −1 charged 1,3-dibutylimidazolidine-2,4,5-trithione) with polyfunctional phosphines: tp [tp = bis(2-diphenylphosphinophenyl)phenylphosphine] and qp [qp = tris(2-diphenylphosphinophenyl)phosphine] produces [Ni(tp)(Bu₄btimdt)] (**1**) and [Ni(qp)(Bu₄btimdt)] (**2**), respectively. X-Ray crystallographic studies show that in both complexes, the nickel ion is coordinated in a trigonal bipyramidal geometry with three P-atoms of the tp and of qp (one of the 'arms' of qp is non-coordinating) ligands occupying three facial sites and with two sulfur atoms of Bu₄btimdt [5,5′-bis(1,3-dibutyl-4-imidazolidine-2-thione-4-thiolate)]. This new S,S dinegative chelating ligand is generated *in situ* by desulfurisation of one of the two vicinal sulfur atoms on each ligand in [Ni(Bu₂timdt)₂] and C–C coupling between the two imidazole rings. The Bu₄btimdt anion is chiral, as free rotation about the C–C bond between the two imidazole rings is hindered by high energy barriers. No desulfurisation is observed when reacting Bu₄N[Ni(dmit)₂] with tp, and the obtained product is [Ni(tp)(dmit)] (**3**), a nickel complex where the metal is still coordinated with a trigonal bipyramidal geometry (three P-atoms of the tp ligand and two sulfur atoms of the dmit ligand).

Introduction

The importance of metal-dithiolene complexes has increased in recent years due to their applications in the field of new molecular materials. Solids that exhibit electrical[1] and magnetic properties,[2] near-infrared dyes,[3] and non-linear optical materials[4] based on metal-dithiolenes have been reported. Interest is also devoted to their reactions which produce sulfur-based heterocyclic systems.[5] Molecules derived from $C_3S_5^{2-}$ (dmit) have received extra attention due to their relevance for the synthesis of new electronic and photonic materials.[6] Rauchfuss *et al.* have shown that the treatment of an acetonitrile solution of a salt of $[Zn(dmit)_2]^{2-}$ with sulfuryl chloride at −40 °C gives rise to a (dmit)₂ dimer, formed by two planar C_3S_5 units interconnected by persulfide bridges, and a (dmit)$_n$ polymeric compound.[7] The redox properties of dmit and related molecules have recently been deeply investigated.[8]

We are extensively investigating the properties of a class of nickel dithiolenes [Ni(R₂timdt)₂], (R₂timdt = −1 charged 1,3-dialkylimidazolidine-2,4,5-trithione) synthesised in our laboratory. The R₂timdt ligand, where N-electron donor atoms of the imidazoline ring are forced into co-planarity with the dithiolene ring, was revealed to be valuable in shifting the low energy transition typical of this class of complexes within a region of interest for near-infrared (NIR) dyes, while stability was maintained.[9]† [Ni(R₂timdt)₂] differs from the structural analog [Ni(dmit)₂] in the presence of the better donor NR

groups instead of sulfur atoms in the penta-atomic ring adjacent to the dithiolene core. These complexes can also provide a convenient route for synthesising new sulfur-based heterocyclic molecules which are difficult to obtain or are unobtainable by conventional methods. The reaction of [Ni(R₂-timdt)₂][9] with dibromine at 0 °C produces a dimer (R₂timdt)₂[10] similar to (dmit)₂, as shown in Scheme 1.

Scheme 1
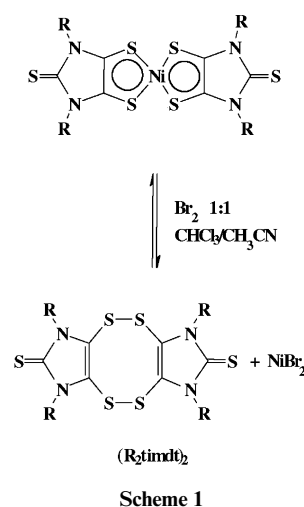
(R₂timdt)₂ is a stable molecule that can be stored and used as a very convenient source of the ligand to prepare metal–dithiolene complexes since the reductive cleavage of the S–S bonds easily occurs without alteration of the molecule. In this case this is particularly relevant due to the fact that R₂timdt

---

† The neutral complexes absorb very strongly at approximately 1000 nm, a region of special interest for NIR-dyes for their use in Q-switching neodymium lasers. Moreover these complexes work as switchable NIR-dyes, since the absorption is shifted to approximately 1400 nm on reversible reduction.

ligands cannot be isolated when non-coordinated. For this reason, the nickel-complexes are prepared by the *in situ* sulfurisation reaction of the 1,3-dialkylimidazolidine-2-thione-4,5-dione in the presence of the metal. The sulfurisation of this vicinal dione, in the absence of nickel, following a procedure which works well to prepare six- and seven-membered cyclic dithiooxamides, does not produce the foreseen 1,3-dialkyl-imidazolidine-2,4,5-trithione, but 4,5,6,7-tetrathiocino[1,2-*b*: 3,4-*b'*]diimidazolyl-1,3,8,10-tetraalkyl-2,9-dithione (R$_4$todit, shown in Scheme 2).[11]
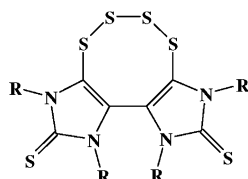

Scheme 2 R$_4$todit.

A C–C coupling between two imidazole rings and the formation of an octa-atomic ring containing four sulfur atoms connected through persulfide bonds is achieved. This molecule, which has relevant properties as an anticancer agent,[12] is, in contrast to (R$_2$timdt)$_2$, unsuitable as a source of ligands in the preparation of metal-dithiolenes.

R$_4$todit are electro-active heterocycles and undergo reduction and elimination of two sulfur atoms by reacting with an alcoholate and new anions R$_4$btimdt [5,5′-bis(1,3-dialkyl-4-imidazolidine-2-thione-4-thiolate] are obtained. These anions have been trapped in the complex [Ni(dppe)(R$_4$btimdt)] if [Ni-(dppe)Cl$_2$] [dppe = 1,2-bis(diphenylphosphino)ethane] is added to the above mentioned reaction mixture, buffered with ammonium acetate. R$_4$btimdt is oxygen sensitive and from its solution left open to the air, a trimer, where persulfide bridges connect three R$_4$btimdt units, has been isolated as oxidation product.[13] R$_4$btimdt is also unexpectedly obtained from [Ni(R$_2$timdt)$_2$][9] when reacting these complexes with polyfunctional phosphines as described here.

Results and discussion

The reaction of [Ni(Bu$_2$timdt)$_2$] with mono-(Ph$_3$P) or bi-functional (dppe) phosphines leaves the reagents unchanged (see details in Experimental section). Unexpectedly the same reaction with polyfunctional phosphines [tp = bis(2-diphenyl-phosphinophenyl)phenylphosphine], and qp [qp = tris(2-diphenylphosphinophenyl)phosphine] produces [Ni(tp)(Bu$_4$-btimdt)] (**1**) and [Ni(qp)(Bu$_4$btimdt)] (**2**), respectively, according to Scheme 3.

The molecular structures of **1** and of **2**, which lack butyl and non-bridging phenyl groups for clarity, are reported in Fig. 1 and 2, respectively, with the corresponding atom-labelling scheme and selected bond lengths and angles collected in Tables 1 and 2. A brief description of **1** has been reported previously.[13] In both complexes, the nickel ion is coordinated with a trigonal bipyramidal geometry with three *fac* P atoms of the tp or qp ligands and with two S atoms of the Bu$_4$btimdt ligand. The chelation of tp and qp results in the formation of two penta-atomic rings showing an 'envelope' conformation. Both tp and qp behave as tripodal ligands, since one of the 'arms' of qp is not coordinating. This behaviour can be explained considering that in five-coordinated nickel(II) complexes an 18e$^-$ configuration is reached, and that Bu$_4$btimdt is unsuitable as a mono-coordinated ligand. An 'arm off' coordination by polypodal phosphines has been observed in the case where an 18e$^-$ trigonal bipyramidal species goes to a 16e$^-$ square one.[14] Fluxionality and arm-off reactions of octahedral rhodium(III) complexes with tripodal phosphines have been reported.[15] A facile oxidation of the uncoordinated P-atom is predicted.[16] The Ni–P$_{apical}$ distances are shorter than Ni–P$_{equatorial}$ ones, in contrast with a possible elongation of the apical distances due to the *trans* effect of the sulfur atoms of the Bu$_4$btimdt ligand. A similar shortening of the Ni–P$_{apical}$ distance of the central phosphorus of tricoordinated ligands has been previously observed in the complex [NiI$_2$(eptp)] (eptp = PhP(CH$_2$)$_2$-PPh(CH$_2$)$_2$PPh$_2$) and ascribed to the "double chelate effect" of the central phosphorus which is simultaneously part of two five-membered rings.[17] However, since the Ni–S distances also differ, the shorter being that involving the sulfur at the apex
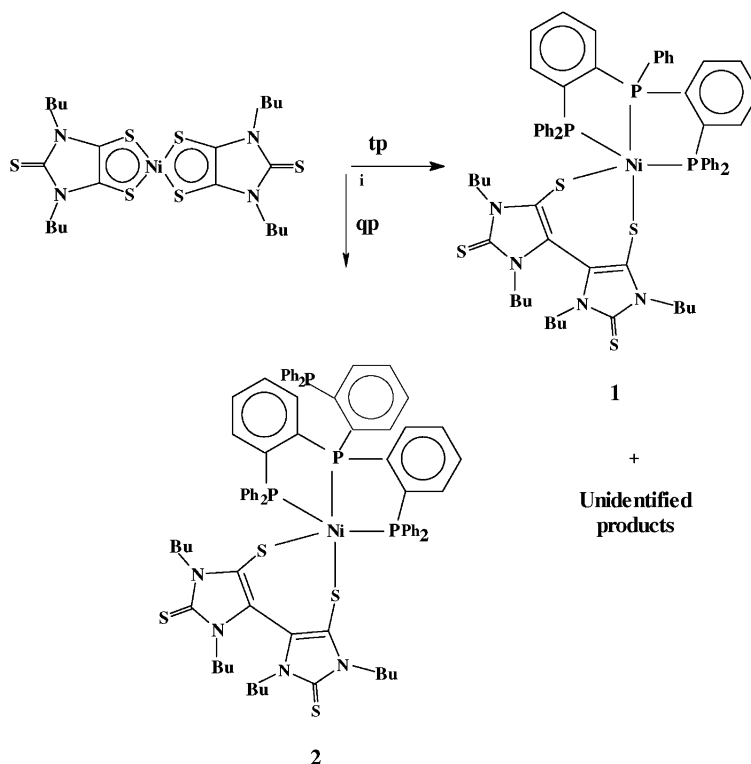
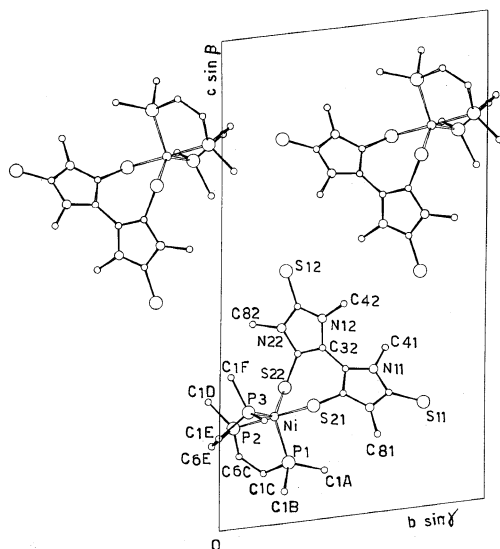**Scheme 3** **i** = tp excess, THF, reflux under N$_2$, 24 h.

Fig. 1 Projection of [Ni(tp)(Bu$_4$btimdt)] (**1**) along *a*. Phenyl rings and butyl chains are omitted for clarity.
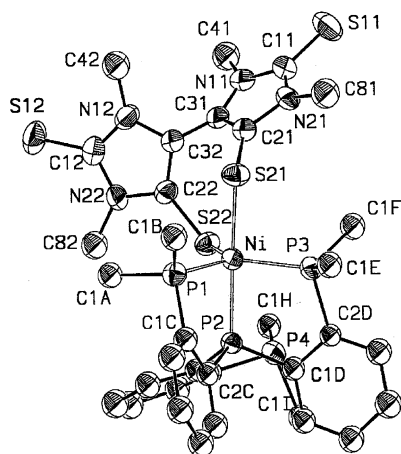

Fig. 2 Molecular structure of [Ni(qp)(Bu$_4$btimdt)] (**2**). Phenyl rings and butyl chains are omitted for clarity.

of the bipyramid, it seems preferable to explain the longer equatorial and shorter bond lengths by using an over-simplified crystal field model which has been proposed for similar complexes.[18] Accordingly, since in a trigonal bipyramidal d^8 configuration, the d_{z^2} is unoccupied being destabilised compared with other orbitals, shorter axial and longer equatorial bond lengths will produce an increase in the energy of the unoccupied d_{z^2} orbital and a stabilisation of the occupied orbitals. As cited above, the Bu$_4$btimdt dianion acts as a bidentate ligand being coordinated to the metal through the two thiolato sulfur atoms, in such a way that a hepta-atomic ring showing a pseudo two fold-axis (including the metal) results. This ligand is generated *in situ* for elimination of one of the two vicinal sulfur atoms on each R$_2$timdt coordinated to the metal in the nickel complex with a coupling of two imidazole rings through the formation of a C–C single bond similarly to what happens in the sulfurisation reaction of the 1,3-dialkylimidazolidine-2-thione-4,5-dione to produce R$_4$todit.

The structural parameters of the Bu$_4$timdt anion in compounds **1** and **2** are in good agreement. The two imidazoline rings are planar and their orientation, determined by the mutually opposite disposition of the butyl groups, is indicated by the torsion angle N(11)–C(31)–C(32)–N(12) [−72(1) and −65(2)° for **1** and **2**, respectively]. Of all the butyl groups in compounds **1** and **2** only one, the C(42)–C(5)–C(6)–C(7) group of **2** (the fragment C(5)–C(6)–C(7) is not reported in Fig. 2 for clarity), results in the extended shape. The Bu$_4$btimdt

Table 1 Selected bond lengths [Å] and angles [deg] for [Ni(tp)-(Bu$_4$btimdt)] (**1**)

Ni–P(1)	2.297(3)	P(3)–C(1G)	1.810(10)
Ni–P(2)	2.174(3)	N(11)–C(11)	1.359(11)
Ni–P(3)	2.204(3)	N(11)–C(31)	1.391(10)
Ni–S(21)	2.270(3)	N(11)–C(41)	1.462(12)
Ni–S(22)	2.341(3)	N(21)–C(11)	1.350(11)
S(11)–C(11)	1.693(8)	N(21)–C(21)	1.401(9)
S(21)–C(21)	1.716(8)	N(21)–C(81)	1.461(11)
S(12)–C(12)	1.701(9)	N(12)–C(12)	1.380(11)
S(22)–C(22)	1.746(8)	N(12)–C(32)	1.407(10)
P(1)–C(1C)	1.838(9)	N(12)–C(42)	1.441(12)
P(1)–C(1A)	1.837(8)	N(22)–C(12)	1.340(11)
P(1)–C(1B)	1.820(8)	N(22)–C(82)	1.456(12)
P(2)–C(6C)	1.823(8)	N(22)–C(22)	1.392(9)
P(2)–C(6E)	1.825(9)	C(21)–C(31)	1.371(11)
P(2)–C(1D)	1.805(9)	C(31)–C(32)	1.446(11)
P(3)–C(1E)	1.825(9)	C(22)–C(32)	1.350(11)
P(3)–C(1F)	1.813(8)		
P(2)–Ni–P(1)	84.74(9)	C(11)–N(11)–C(31)	110.1(7)
P(3)–Ni–P(1)	118.37(9)	C(11)–N(11)–C(41)	125.8(8)
P(2)–Ni–P(3)	84.33(9)	C(31)–N(11)–C(41)	124.1(8)
P(2)–Ni–S(21)	169.94(10)	C(11)–N(21)–C(21)	111.4(7)
P(3)–Ni–S(21)	85.95(10)	C(11)–N(21)–C(81)	122.9(7)
S(21)–Ni–P(1)	97.65(9)	C(21)–N(21)–C(81)	125.7(7)
P(2)–Ni–S(22)	88.36(9)	C(12)–N(12)–C(32)	107.9(7)
P(3)–Ni–S(22)	136.46(10)	C(12)–N(12)–C(42)	123.9(8)
S(21)–Ni–S(22)	100.50(9)	C(32)–N(12)–C(42)	127.4(8)
P(1)–Ni–S(22)	103.51(9)	C(12)–N(22)–C(82)	125.1(8)
C(21)–S(21)–Ni	111.8(3)	C(12)–N(22)–C(22)	110.5(7)
C(22)–S(22)–Ni	106.6(3)	C(82)–N(22)–C(22)	124.4(8)
C(1C)–P(1)–C(1A)	102.7(4)	N(21)–C(11)–N(11)	105.7(7)
C(1C)–P(1)–C(1B)	103.1(4)	N(21)–C(11)–S(11)	127.6(7)
C(1A)–P(1)–C(1B)	103.5(4)	N(11)–C(11)–S(11)	126.8(7)
C(1C)–P(1)–Ni	106.2(2)	C(31)–C(21)–N(21)	105.1(7)
C(1A)–P(1)–Ni	122.7(3)	C(31)–C(21)–S(21)	130.4(6)
C(1B)–P(1)–Ni	116.2(3)	N(21)–C(21)–S(21)	124.4(6)
C(6C)–P(2)–C(6E)	104.9(4)	C(21)–C(31)–N(11)	107.6(7)
C(6C)–P(2)–C(1D)	106.2(4)	C(21)–C(31)–C(32)	124.8(7)
C(6E)–P(2)–C(1D)	104.4(4)	N(11)–C(31)–C(32)	127.0(8)
C(6C)–P(2)–Ni	109.5(2)	N(22)–C(12)–N(12)	106.9(7)
C(6E)–P(2)–Ni	106.0(3)	N(22)–C(12)–S(12)	127.5(7)
C(1D)–P(2)–Ni	124.2(3)	N(12)–C(12)–S(12)	125.6(7)
C(1E)–P(3)–C(1F)	105.0(4)	C(32)–C(22)–N(22)	106.9(7)
C(1E)–P(3)–C(1G)	103.8(4)	C(32)–C(22)–S(22)	127.4(6)
C(1F)–P(3)–C(1G)	103.8(4)	N(22)–C(22)–S(22)	125.7(7)
C(1E)–P(3)–Ni	106.2(3)	C(22)–C(32)–N(12)	107.8(7)
C(1F)–P(3)–Ni	115.6(3)	C(22)–C(32)–C(31)	127.2(8)
C(1G)–P(3)–Ni	120.9(3)	N(12)–C(32)–C(31)	125.0(8)

is chiral, the free rotation about C(31)–C(32) being hindered by high energy barriers,[19] which result from contacts S $\cdots$ C$_{butyl}$, C$_{butyl}$ $\cdots$ C$_{butyl}$. The value of the torsion angle C(21)–C(31)–C(32)–C(22) observed for the chelating ligand [±58(1) and ±57(1)° for **1** and **2**, respectively] is exactly the same as calculated for the free ligand at the minimum of energy [±57(1)°]. These values also indicate that the enantiomers of the free ligand can be isolated. Therefore **1** and **2** are chiral, but both enantiomers are present in the crystals.
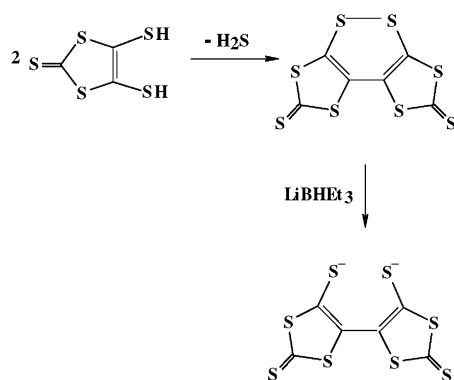
The 1,3-dithiole ring based counterpart of the R$_4$btimdt dianion: C$_6$S$_8^{2-}$, has been prepared *via* the reactions shown in Scheme 4 and used to prepare Ni(II) complexes.[20]

In order to check whether or not the desulfurisation reaction induced by tp also works with dmit-based nickel-dithiolenes to form C$_6$S$_8^{2-}$, we have allowed (Bu$_4$N)[Ni(dmit)$_2$] to react with tp according to Scheme 5.

In the obtained product [Ni(tp)(dmit)] (**3**) the dmit ligand is recovered unchanged. The nickel ion is coordinated similarly as in **1** and **2** with a trigonal bipyramidal geometry with three *fac* P atoms of the tp ligand and with two S atoms of the dmit ligand (see Fig. 3, selected bond lengths and angles are in Table 3). The coordination to the metal through the two thiolato sulfur atoms of the dmit ligand produces a penta-atomic ring (including the metal) showing an envelope conformation. The dmit anion is

**Table 2** Selected bond lengths [Å] and angles [deg] for [Ni(qp)-(Bu₄btimdt)] (**2**)

Ni–P(1)	2.246(3)	S(21)–C(21)	1.757(10)
Ni–P(2)	2.188(2)	S(12)–C(12)	1.693(10)
Ni–P(3)	2.199(3)	S(22)–C(22)	1.734(9)
Ni–S(21)	2.291(2)	N(11)–C(11)	1.343(12)
Ni–S(22)	2.344(3)	N(11)–C(31)	1.425(12)
P(1)–C(1B)	1.813(6)	N(11)–C(41)	1.431(13)
P(1)–C(1C)	1.806(5)	N(21)–C(11)	1.381(14)
P(1)–C(1A)	1.822(6)	N(21)–C(81)	1.434(13)
P(2)–C(1D)	1.819(4)	N(21)–C(21)	1.431(12)
P(2)–C(1G)	1.842(4)	N(12)–C(12)	1.365(12)
P(2)–C(2C)	1.840(5)	N(12)–C(32)	1.392(10)
P(3)–C(1E)	1.819(5)	N(12)–C(42)	1.414(12)
P(3)–C(1F)	1.813(6)	N(22)–C(12)	1.358(12)
P(3)–C(2D)	1.850(5)	N(22)–C(22)	1.407(10)
P(4)–C(1H)	1.842(5)	N(22)–C(82)	1.442(12)
P(4)–C(1I)	1.849(5)	C(21)–C(31)	1.312(12)
P(4)–C(2G)	1.864(5)	C(31)–C(32)	1.421(12)
S(11)–C(11)	1.686(11)	C(22)–C(32)	1.365(12)
P(2)–Ni–P(1)	85.68(9)	C(22)–S(22)–Ni	109.5(3)
P(3)–Ni–P(1)	123.21(10)	C(11)–N(11)–C(31)	109.4(8)
P(2)–Ni–P(3)	85.70(9)	C(11)–N(11)–C(41)	124.0(9)
P(2)–Ni–S(21)	168.03(10)	C(31)–N(11)–C(41)	126.6(8)
P(3)–Ni–S(21)	90.24(10)	C(11)–N(21)–C(81)	124.0(9)
P(1)–Ni–S(21)	87.15(10)	C(11)–N(21)–C(21)	107.8(7)
P(2)–Ni–S(22)	91.43(8)	C(81)–N(21)–C(21)	127.7(10)
P(3)–Ni–S(22)	117.24(10)	C(12)–N(12)–C(32)	109.6(7)
P(1)–Ni–S(22)	119.00(10)	C(12)–N(12)–C(42)	124.2(8)
S(21)–Ni–S(22)	100.43(9)	C(32)–N(12)–C(42)	125.5(8)
C(1B)–P(1)–C(1C)	103.7(3)	C(12)–N(22)–C(22)	110.3(7)
C(1B)–P(1)–C(1A)	104.1(4)	C(12)–N(22)–C(82)	123.8(8)
C(1C)–P(1)–C(1A)	103.7(3)	C(22)–N(22)–C(82)	125.9(8)
C(1B)–P(1)–Ni	120.1(3)	N(11)–C(11)–N(21)	107.0(8)
C(1C)–P(1)–Ni	105.3(2)	N(11)–C(11)–S(11)	126.2(9)
C(1A)–P(1)–Ni	117.9(2)	N(21)–C(11)–S(11)	126.7(8)
C(1D)–P(2)–C(1G)	108.8(3)	C(31)–C(21)–N(21)	108.0(9)
C(1D)–P(2)–C(2C)	102.4(3)	C(31)–C(21)–S(21)	130.2(8)
C(1G)–P(2)–C(2C)	105.3(3)	N(21)–C(21)–S(21)	121.8(7)
C(1D)–P(2)–Ni	111.31(19)	C(21)–C(31)–N(11)	107.8(8)
C(1G)–P(2)–Ni	119.9(2)	C(21)–C(31)–C(32)	128.5(9)
C(2C)–P(2)–Ni	107.49(19)	N(11)–C(31)–C(32)	123.2(8)
C(1E)–P(3)–C(1F)	107.3(3)	N(12)–C(12)–N(22)	106.2(8)
C(1E)–P(3)–C(2D)	99.9(3)	N(12)–C(12)–S(12)	126.0(8)
C(1F)–P(3)–C(2D)	104.1(3)	N(22)–C(12)–S(12)	127.7(8)
C(1E)–P(3)–Ni	115.1(3)	C(32)–C(22)–N(22)	105.9(7)
C(1F)–P(3)–Ni	117.9(2)	C(32)–C(22)–S(22)	130.1(7)
C(2D)–P(3)–Ni	110.43(19)	N(22)–C(22)–S(22)	123.9(6)
C(1H)–P(4)–C(1I)	100.4(3)	C(22)–C(32)–N(12)	107.7(7)
C(1H)–P(4)–C(2G)	106.1(3)	C(22)–C(32)–C(31)	126.1(7)
C(1I)–P(4)–C(2G)	100.0(3)	N(12)–C(32)–C(31)	126.2(7)
C(21)–S(21)–Ni	112.4(3)		

Table 3 Selected bond lengths [Å] and angles [deg] for [Ni(tp)-(dmit)] (**3**)

Ni–P(1)	2.241(2)	S(3)–C(1)	1.747(4)
Ni–P(2)	2.146(1)	S(3)–C(3)	1.729(5)
Ni–P(3)	2.216(1)	S(4)–C(2)	1.748(4)
Ni–S(1)	2.240(1)	S(4)–C(3)	1.721(5)
Ni–S(2)	2.347(1)	S(5)–C(3)	1.653(4)
S(1)–C(2)	1.747(4)	C(1)–C(2)	1.340(6)
S(2)–C(1)	1.738(4)		
P(1)–Ni–P(2)	86.72(4)	C(1)–S(3)–C(3)	98.4(2)
P(1)–Ni–P(3)	129.47(4)	C(2)–S(4)–C(3)	98.1(2)
P(1)–Ni–S(1)	90.21(5)	S(2)–C(1)–S(3)	120.1(2)
P(1)–Ni–S(2)	107.74(5)	S(2)–C(1)–C(2)	124.7(3)
P(2)–Ni–P(3)	86.38(4)	S(3)–C(1)–C(2)	115.2(3)
P(2)–Ni–S(1)	174.93(5)	S(1)–C(2)–S(4)	120.2(2)
P(2)–Ni–S(2)	93.07(4)	S(1)–C(2)–C(1)	123.4(3)
P(3)–Ni–S(1)	92.48(5)	S(4)–C(2)–C(1)	116.3(3)
P(3)–Ni–S(2)	122.58(5)	S(3)–C(3)–S(4)	111.9(2)
S(1)–Ni–S(2)	91.71(4)	S(3)–C(3)–S(5)	124.2(3)
Ni–S(1)–C(2)	99.12(14)	S(4)–C(3)–S(5)	123.9(3)
Ni–S(2)–C(1)	96.69(13)		
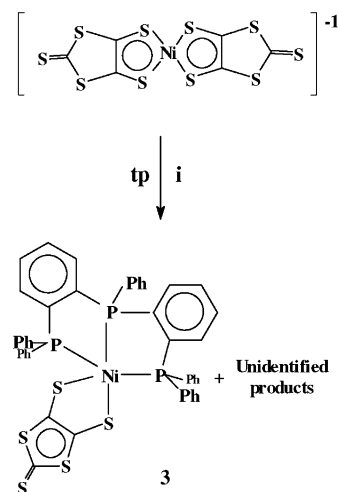
Scheme 5   **i** = tp excess, THF, reflux under N₂, 24 h.
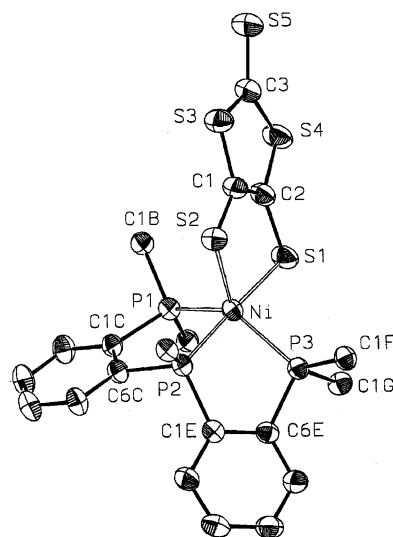
Fig. 3 Molecular structure of [Ni(tp)(dmit)] (**3**). Phenyl rings are omitted for clarity. The unlabelled carbon atom connected to P(1) belongs to the phenyl ring A, which is disordered.

Scheme 4

nearly planar (dev. max = 0.027(2) Å). As observed in **1** and **2**, the apical Ni–P and Ni–S distances are shorter than the equatorial ones. While metal complexes containing phosphorus and dithiolene ligands have been known for a long time,[21–23] structurally characterised examples are uncommon and among them the square-planar [M(dppe)(dmit)][24] (M=Ni, Pd and Pt)

and the six coordinate [W(CO)₂(dmit)L₂][25] (L₂ = (PR₃)₂ and dppe) have been reported. Bond distances of dmit fragments in these complexes are in accordance with those in **3** where dmit works similarly as a dianion. Raman scattering has been shown to be highly suitable to correlate the C=C frequency and the

charge for the $[M(dmit)_2]^{n-}$ ($n = 0, 0.29, 0.5, 1, 2$; M = Ni, Pd) case,[26] and $[Ni(Pr^i_2timdt)(dmit)]^{n-}$ compounds ($Pr^i = $ *iso*-propyl, $n = 0$; $n = 1$).[27] A Raman peak which can be assigned to the C=C stretching vibration for **3** has been observed at 1450 cm^{-1} and is reported in Fig. 4. The position of this band, very close to the frequency of the C=C peak for $[Ni(dmit)_2]^{-2}$, Fig. 5, suggests a
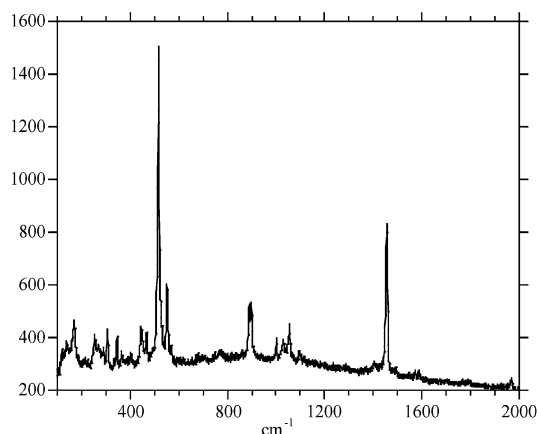

Fig. 4 The Raman spectrum of a single crystal of **3**.

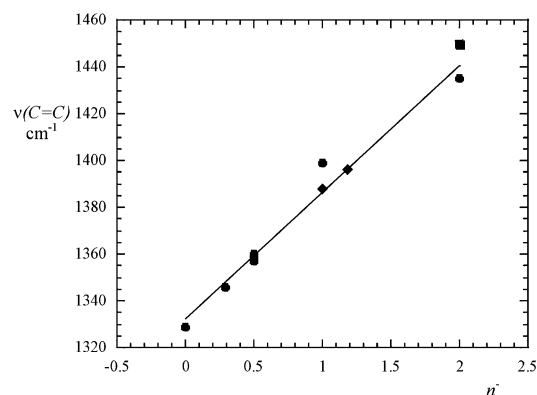**Fig. 5** Linear correlation of the totally symmetric C=C stretching vibration against the charge ($n-$) for $[Ni(dmit)_2^{n-}]$ (●), $[Ni(Pr^i_2$-timdt)(dmit)$^{n-}]$ (◆). The peak at 1450 cm^{-1} assigned to the C=C stretching vibration for **1** is reported in this correlation (■).

double negative charged dithiolene ligand is in accordance with structural results. **1**, **2** and **3** (Fig. 6) show similar electronic spectra characterised in the visible region by the presence of one well resolved peak (in parenthesis: $\varepsilon = $ dm^3 mol^{-1} cm^{-1}, compound) at 568 (8400, **1**), 578 (8000, **2**) and 557 nm (6900, **3**) and shoulders (sh) or peak at 430 (**1**), 416–500 (**2**) (sh) and 492 nm (5900, **3**). In the UV-region an intense peak with a shoulder or a broad band are observed in the 280–350 nm region [280 (sh, ε ~29200), 325 sh (~25500), **1**; 280 (41600), **2**; 299
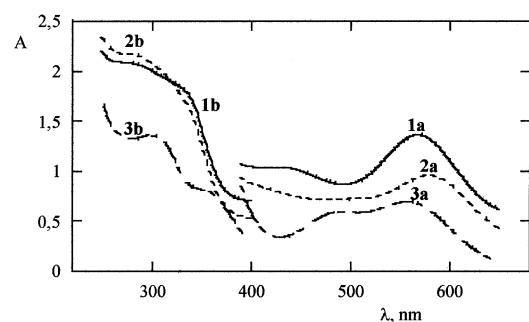

Fig. 6 Absorption spectra of 1.0×10^{-4} mol dm^{-3} CH$_2$Cl$_2$ solutions of **1**, **2**, **3**; silica cell 0.5 cm in the 230–400 nm range (suffix **b**) and 1.0 cm in the 400–700 nm range (suffix **a**). The absorbance scale refers to **3**, while it is translated by 0.2 and 0.4 units for spectra of **2** and **3**, respectively, to avoid overlapping spectra.

(27200), 352 sh (~16200), **3**]. These spectra are similar to those of trigonal bipyramidal complexes of nickel(II) coordinated with polypodal phosphorus ligands, and the assignments of the electronic spectra of trigonal-pyramidal Ni-complexes have been established for a long time.[28] ‡ Following these assignments, the bands found at lower frequencies should be mainly due to the $d_{x^2-y^2}$, $d_{xy} \longrightarrow d_z^2$ and to d_{xz}, $d_{yz} \longrightarrow d_z^2$ transitions, while the strong bands in the 280–350 nm region may be assigned to P $\longrightarrow$ Ni and S $\longrightarrow$ Ni CTLM transitions. As previously observed in Ni(II) trigonal bipyramidal complexes with polyfunctional phosphines, these peaks show unusually high intensity for d–d transitions. Their intensity has been explained taking into account a large mixture of higher configurations by odd crystal-field components.[28b]

In summary, by reacting nickel dithiolenes belonging to the class of $[Ni(R_2timdt)_2]$ complexes with the polyfunctional phosphines tp and qp a novel desulfurisation reaction with concomitant C–C coupling between two imidazoline rings and production of a new class of dithiolate ligands ($R_4btimdt$) has been achieved. No dmit based counterpart of the $R_4btimdt$ ligand is formed by this route, and this could be ascribed to the different capability of the two rings adjacent to the dithiolene-core to give C–C coupling. Imidazole rings have been shown to be able to undergo C–C coupling easily, as reported above, in ref. 11 by us and as observed by Rauchfuss *et al.* when reacting 1-methylimidazole (MeIm) to produce a methylimidazolium salt of the anion $C_6H_2N_4S_4Me^{2-}$.[29] Further experimental and theoretical work is required to explain this behaviour. The potential of metal-dithiolene complexes to work as precursors of sulfur-rich donors seems high in order to provide alternative routes for synthesising new ligands, which are not easily attained or are unobtainable by conventional routes, and have potential interest in several fields of chemistry (material, medicinal and coordination chemistry).

Experimental

Reagents and solvents of reagent grade quality were used as supplied by Aldrich. The polyphosphines tp and qp were prepared according to reference 30.

Reaction with PPh$_3$

$[Ni(Bu_2timdt)_2]$ (0.06 g; 0.1 mmol) and PPh$_3$ (0.06 g; 0.12 mmol) (1 : 1 molar ratio) were mixed and refluxed in THF (100 mL) under N$_2$ for 24 h. The colour of the reaction mixture remained unchanged. After one day the refluxing was stopped, and, on cooling, the reagents precipitated from the reaction mixture. Further amounts of reagents to an almost quantitative recovery were obtained from the filtrate by rotary-evaporation. No reaction was also observed with other $[Ni(R_2timdt)_2]$ complexes on varying the R groups.

Reaction with dppe

$[Ni(Bu_2timdt)_2]$ (0.06 g; 0.1 mmol) and dppe (0.16 g; 0.4 mmol) (1 : 4 molar ratio) were mixed and refluxed in THF (100 mL) under N$_2$ for 24 h. Following the same procedure described above, the reagents were recovered unchanged.

Synthesis of 1

$[Ni(Bu_2timdt)_2]$ (0.05 g; 0.08 mmol) and an excess of tp (0.20 g; 0.3 mmol) (1 : 4 molar ratio) were mixed and refluxed in THF

‡ One low energy band derived from the transition $^1E' \longrightarrow {}^1A_1$ [$d_{x^2-y^2}$, d_{xy} (e$'$) $\longrightarrow d_z^2(a_1')$] in D_{3h} symmetry is expected. A second band $^1E'' \longrightarrow {}^1A_1$ [d_{xz}, d_{yz} (e$''$) $\longrightarrow d_z^2(a_1')$], electronically forbidden in D_{3h}, becomes allowed in C_{3v} symmetry. These peaks are expected to be split on going to low symmetry. In the 200–400 nm region charge-transfer ligand-to-metal transitions are expected.

Table 4 Crystallographic data of compounds **1**–**3**

Compound	[Ni(tp)(Bu$_4$btimdt)] (**1**)	[Ni(qp)(Bu$_4$btimdt)] (**2**)	[Ni(tp)(dmit)] (**3**)
Chemical formula	C$_{64}$H$_{69}$N$_4$NiP$_3$S$_4$	C$_{76}$H$_{78}$N$_4$NiP$_4$S$_4$	C$_{45}$H$_{33}$NiP$_3$S$_5$
M	1174.09	1358.25	885.63
Crystal system	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)
a/Å	11.057(4)	16.689(5)	9.541(6)
b/Å	12.973(6)	23.461(5)	21.873(5)
c/Å	23.023(9)	18.253(5)	19.730(5)
α/deg	78.69(2)		
β/deg	75.88(2)		99.97(2)
γ/deg	69.89(2)		
V/Å^3	2985(2)	7147(3)	4055(3)
Z	2	4	4
Wavelength, λ/Å	Cu-Kα(1.541838)	Cu-Kα(1.541838)	Cu-Kα(1.541838)
T/K	293(2)	293(2)	293(2)
μ/cm^{-1}	28.66	26.72	44.70
Reflns collected	11289	7015	7886
Ind. reflns	11289	7015	7665
$R[I > 2\sigma(I)]$	0.0867	0.0666	0.0584
wR_2(all data)	0.3316	0.1925	0.1842

(50 mL), under N$_2$ for 24 h. The solution turned from olive-green to purple. The solvent was removed *in vacuo* and by repeated recrystallization of the crude product from CH$_3$CN–Et$_2$O a complete separation of **1** from the excess of the less soluble tp was achieved. Well-shaped shiny red–brown crystals (0.07 g; 72% yield) of **1**, suitable for X-ray studies, were obtained. Anal. Found: C, 65.72; H 6.53; N 4.66; S 10.22; Calc. for C$_{64}$H$_{69}$N$_4$NiP$_3$S$_4$: C, 65.47; H 5.92; N 4.77; S 10.92%; IR (cm^{-1}): 3050w, 2960mw, 2940mw, 2860w, 1480mw, 1430m, 1405s, 1385ms, 1355mw, 1300w, 1260w, 1220m, 1115m, 1100m, 1070w, 1030w, 1000w, 940w, 770w, 740s, 695s, 680w, 670w, 620w, 545s, 530s, 510ms, 480w, 470w; Raman (cm^{-1}): 1615 ms, 1575w, 1525m, 1401ms, 1420sh, 1285w, 1256w, 1100w, 1000w, 750w, 720w, 675vw, 525w, 575w, 420s, 310m; UV-Vis. [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 280 sh (~29200), 325 sh (~25500), 430 sh, 490sh, 568 (8400), 744 (1400), 875 (1400).

Synthesis of 2

[Ni(Bu$_2$timdt)$_2$] (0.1 g; 0.5 mmol) and an excess of qp (0.536 g; 2 mmol) (1 : 4 molar ratio) were mixed and refluxed in THF (100 mL), under Ar for 24 h. The solution turned from olive-green to dark blue: after filtration to remove at first the excess of qp the solvent was evaporated *in vacuo* and the crude product recrystallized once from CH$_3$CN–Et$_2$O in freezer and twice from CH$_3$CN–THF at room temperature in order to achieve a complete separation of **2** from the excess of the less soluble qp. Well-shaped shiny dark blue crystals (0.114 g, 13% yield) of **2**, suitable for X-ray studies, were obtained. Anal. Found: C, 67.64; H, 6.32; N, 4.10; S, 8.38; Calc. for C$_{76}$H$_{78}$N$_4$NiP$_4$S$_4$: C, 67.19; H, 5.79; N, 4.13; S, 9.45%. IR (cm^{-1}) 3051m, 2995ms, 2930ms, 2867m, 1737w, 1620w, 1479w, 1432m, 1401s, 1383ms, 1351mw, 1293w, 1253w, 1213m, 1185w, 1113m, 1095m, 1048w, 1027w, 935w, 843vw, 742s, 694s, 673mw, 652vw, 544s, 526s, 509s; Raman (cm^{-1}): 1623mw, 1538mw, 1405mw, 1384mw, 546w, 488w, 419s, 313m, 292mw, 244m, 238m, 159s; UV-Vis. [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 280 (41600), 416 sh, 502 sh, 578 (8000), 799 (2100).

Synthesis of 3

Bu$_4$N[Ni(dmit)$_2$][6] (0.1 g; 0.5 mmol) and an excess of tp (0.364 g; 2 mmol) (1 : 4 molar ratio) were mixed and refluxed in THF (100 mL), under Ar for 24 h. The solution turned from olive-green to purple: after filtration to remove at first the excess of tp the solvent was evaporated and the crude product recrystallized from CH$_3$CN–THF at room temperature by standing. After 4 days well-shaped shiny dark red crystals (0.091 g, 71% yield) of

3, suitable for X-ray studies, were obtained. Anal. Found: C, 60.18; H, 3.83; N, 0.60; S, 17.97; Calc. for C$_{45}$H$_{33}$NiP$_3$S$_5$·1/2 CH$_3$CN: C, 60.97; H, 3.84; N, 0.77; S, 17.69%; IR (cm^{-1}): 3051m, 2995ms, 2930ms, 2867m, 1737w, 1620w, 1479w, 1432m, 1401s, 1383ms, 1351mw, 1293w, 1253w; Raman (cm^{-1}): 1453ms, 1055w, 1025w, 1000w, 901mw, 891mw, 551mw, 514s, 467w, 446w, 304w; UV-Vis. [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: 299 (27200), 352sh (~16200), 492 (5900), 557 (6900).

Raman spectra

Raman spectra were carried out at room temperature on single crystals using a LABRAM Jobin-Yvon spectrometer equipped with an integrated microscope (BX 40, Olimpus) for micro Raman measurements. The excitation wavelength was a He–Ne (632.8 nm, 20 mW) laser, the laser power being reduced by a factor 100 in order to avoid sample damage and degradation. A 100x Objective has been used for the injection of laser line and collection of Raman signal in back scattering configuration. The laser line is removed by an holographic super notch filter and the Raman signal is dispersed by a stigmatic 300 mm focal length spectrometer equipped with two exchangeable gratings. A 1800 l/mm grating was used for obtaining the maximum in term of spectral resolution. The signal is finally detected by a CCD 1024 × 256 pixels cooled by a TE Peltier. The scattering peaks were calibrated against a Si standard (v = 520 cm^{-1}). No sample decomposition was observed during the experiments.

IR spectra

IR spectra (4000–200 cm^{-1}) were recorded on KBr pellets with a Perkin Elmer mod. 983 spectrometer.

Electronic spectra

Electronic spectra were recorded at room temperature in CH$_2$Cl$_2$ solutions ($c = 1.0 \times 10^{-4}$ mol dm^{-3}) in the 200–1000 nm range, in 0.5 and 1.0 cm silica cells with a Cary 5 Spectrophotometer.

Crystal structure determination

Crystal data and the most relevant parameters adopted in the X-ray data collections and refinements are reported in Table 4. Diffraction data were collected at room temperature on a Enraf-Nonius CAD4 and on a Siemens AED diffractometer for **1** and **2**–**3** compounds, respectively. The lattice parameters were obtained by least-squares analysis of the setting angle of 29, 30,

and 32 carefully centered reflections choosed from diverse regions of reciprocal spaces in the ranges 18–30, 19–38, and 18–40 ° for **1**–**3**, respectively. The check of the standard reflections showed no significant decrease. The space groups were chosen on the basis of the systematic extinction and of intensity statistics. The intensities recorded by the θ–2θ scan technique, were corrected for Lorentz and polarization factors. An absorption correction was applied after the last isotropic refinement cycle following the empirical method by Walker and Stuart,[31] for **3** (maximum and minimum values for the transmission factors: 1.000 and 0.697); the corresponding attempts for **1** and **2** were unsuccessful. The structures were solved using direct methods (Sir92[32]) and refined by the full-matrix least-squares on F^2 with SHELXL-97,[33] first with isotropic thermal parameters and then with anisotropic thermal parameters for non-hydrogen atoms, excluding the carbon atoms of the butyl groups of **1** and **2** and those of the disordered phenyl ring A of **3**. The butyl groups have a large thermal motion, indicating the presence of severe disorder. Attempts to split the carbon atoms in "partial" atoms were unsuccessful. Rigid-body constraints were introduced for these groups, for the phenyl rings of **2**, and for the two images of the phenyl ring A of **3** (occupancy factor: 0.6 and 0.4, respectively). All the hydrogen atoms were introduced from geometrical calculations and refined using a riding model. Compound **2** crystallizes in the space group $Pca2_1$, however a Flack[34] parameter of $-0.05(3)$ confirms the absolute structure.

The not so satisfactory values for **1** and **2** result from the bad quality of the crystals (most of them were twinned), as well as from the above mentioned disorder. Atomic scattering factors and the anomalous scattering coefficients were taken from International Tables for X-ray Crystallography[35] The final geometries were analysed by the program PARST97[36] and the drawings were made with ZORTEP.[37] All calculations were carried out on the ENCORE 91 and DIGITAL AlphaStation 255 computers of the CSSD of the C. N. R. Parma. Selected bond lengths and angles are reported in Tables 2,3, and 4 for **1**–**3**, respectively.

CCDC reference numbers 102390, 171252 and 171253.

See http://www.rsc.org/suppdata/dt/b1/b108471b/ for crystallographic data in CIF or other electronic format.

Acknowledgements

References

1 P. Cassoux and L. Valade, *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, John Wiley & Sons, Chichester, 1996, 2nd edn.; H. Tanaka, Y. Okano, H. Kobayashi, W. Suzuki and A. Kobayashi, *Science*, 2001, **291**, 285.

2 A. T. Coomber, D. Beljonne, R. H. Friend, J. K. Brédas, A. Charlton, N. Robertson, A. E. Underhill, M. Kurmoo and P. Day, *Nature*, 1996, **380**, 144.

3 U. T. Mueller-Westerhoff, B. Vance and D. I. Yoon, *Tetrahedron*, 1991, **47**, 909.

4 C. S. Winter, C. A. S. Hill and A. E. Underhill, *Appl. Phys. Lett.*, 1991, **58**, 107.

5 N. Svenstrup and J. Becker, *Synthesis*, 1995, 215; P. J. Nigrey, *Synth. React. Met.-Org. Chem.*, 1986, **16**, 1351.

6 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. H. Clark and A. E. Underhill, *Coord. Chem. Rev.*, 1991, **110**, 115; I. Malfant, N. Cordente, P. G. Lacroix and C. Lepetit, *Chem. Mater.*, 1991, **10**, 4079.

7 X. Yang, T. B. Rauchfuss and S. Wilson, *J. Chem. Soc., Chem. Commun.*, 1990, 34.

8 J. G. Breitzer, A. I. Smirnov, L. F. Szczepura, S. R. Wilson and T. B. Rauchfuss, *Inorg. Chem.*, 2001, **40**, 1421.

9 F. Bigoli, P. Deplano, F. A. Devillanova, V. Lippolis, P. J. Lukes, M. L. Mercuri, M. A. Pellinghelli and E. F. Trogu, *J. Chem. Soc., Chem. Commun.*, 1995, 371; F. Bigoli, P. Deplano, F. A. Devillanova, J. R. Ferraro, V. Lippolis, P. J. Lukes, M. L. Mercuri, M. A. Pellinghelli, E. F. Trogu and J. M. Williams, *Inorg. Chem.*, 1997, **36**, 1218; F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, G. Pintus, E. F. Trogu, G. Zonnedda, H. H. Wang and J. M. Williams, *Inorg. Chim. Acta*, 1998, **273**, 175.

10 P. Deplano, M. L. Mercuri, G. Pintus and E. F. Trogu, *Comments Inorg. Chem. (A)*, 2001, **22**, 353.

11 D. Atzei, F. Bigoli, P. Deplano, M. A. Pellinghelli and E. F. Trogu, *Phosphorus Sulfur*, 1988, **37**, 189.

12 A. Pani, E. Pinna, F. Scintu, G. Perra, S. Corrias, E. Trogu, P. Deplano and P. La Colla, *Anticancer Res.*, 1998, **18**, 4429.

13 F. Bigoli, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, G. Pintus and E. F. Trogu, *Chem. Commun.*, 1999, 2093.

14 D. J. Rauscher, E. G. Thaler, J. C. Huffmann and K. G. Caulton, *Organometallics*, 1991, **10**, 2209; E. G. Thaler, K. Folting and K. G. Caulton, *J. Am. Chem. Soc.*, 1990, **112**, 2664.

15 K. Brandt and W. S. Sheldrick, *Chem. Ber.*, 1996, **129**, 1199.

16 C. Bianchini, C. Mealli, A. Meli and M. Sabat, *Inorg. Chem.*, 1984, **23**, 2731; C. Bianchini, C. A. Gilardi, A. Meli and A. Orlandini, *J. Organomet. Chem.*, 1985, **286**, 259.

17 G. Dyer and J. Roscoe, *Inorg. Chem.*, 1996, **35**, 4098.

18 T. L. Blundell and H. M. Powell, *Acta Crystallogr., Sect. B*, 1971, **27**, 2304.

19 M. Nardelli, *A Fortran Routine for Calculating Non-Bonded Potential Energy*, University of Parma, 1996.

20 J.-H. Chou, T. B. Rauchfuss and L. F. Szczepura, *J. Am. Chem. Soc.*, 1998, **120**, 1805.

21 W. P. Mayweg and G. N. Schrauzer, *Chem. Commun.*, 1966, 640.

22 Z.-Q. Tian, J. P. Donahue and R. H. Holm, *Inorg. Chem.*, 1995, **34**, 5568; G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1983, **22**, 1208; J. M. Bevilacqua, J. A. Zuleta and R. Eisenberg, *Inorg. Chem.*, 1994, **33**, 258.

23 G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1982, **21**, 2403.

24 R. Vicente, J. Ribas, X. Solans, M. Font-Altaba, A. Mari, P. De Loth and P. Cassoux, *Inorg. Chim. Acta*, 1987, **132**, 229.

25 P. K. Baker, M. G. B. Drew, E. E. Parker, N. Robertson and A. E. Underhill, *J. Chem. Soc., Dalton Trans.*, 1997, 1429.

26 K. I. Pokhodnya, C. Faulmann, I. Malfant, R. Andreu-Solano, P. Cassoux, A. Mlayah, D. Smirnov and J. Leotin, *Synth. Met.*, 1999, **103**, 2016.

27 F. Bigoli, P. Cassoux, P. Deplano, M. L. Mercuri, M. A. Pellinghelli, G. Pintus, A. Serpe and E. F. Trogu, *J. Chem. Soc., Dalton. Trans.*, 2000, 4639.

28 (*a*) J. W. Dawson, T. J. McLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave and H. B. Gray, *J. Am. Chem. Soc.*, 1974, **96**, 4428; (*b*) M. J. Norgett, J. H. Thornley and L. M. Venanzi, *J. Chem. Soc. A*, 1967, 540; (*c*) A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier Publishing Company, Amsterdam, 1968, pp. 347–349.

29 S. Al-Ahmad, B. Boje, J. Magull, T. B. Rauchfuss and Y. Zheng, *J. Am. Chem. Soc.*, 1995, **117**, 1145.

30 B. Chiswell and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 417 and references therein.

31 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 58; F. Ugozzoli, *Comput. Chem.*, 1987, **11**, 109.

32 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

33 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.

34 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

35 *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, England, 1974, vol. IV, pp. 99–102, 149.

36 M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659.

37 L. Zsolnai and H. Pritzkow, ZORTEP, ORTEP Original Program Modified for PC, University of Heidelberg, Germany, 1994.