S,C- and S,S-coupling *via* dithiolate transfer reactions from tin to nickel complexes†

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Dithiolate tin(IV) complexes [$SnMe_2(SS)$] (SS = 4,5-dimercapto-1,3-dithiol-2-thione, dmit; 1,2-benzene dithiolate, bdt; and 3,4-toluene dithiolate, tdt) are used as transmetallating agents in the reaction with nickel derivatives [$NiBrR'(PR_3)_2$] (R' = mesitylene (Mes) and 2,4,6-trisisopropylphenyl (Trip), and PR_3 = PPh_3 and PPh_2Me). The reaction results in the isolation of different complexes with a great variety of stoichiometries, including mono-, di- and trinuclear nickel complexes with the general formulae: [$Ni(SS)(PR_3)]_2$, [$Ni(Mes)(SS\text{-}Mes)(PR_3)$], [$Ni(SS\text{-}Mes)_2$] and [$Ni_3(bdt)_3(PPh_2Me)_2$], and the organic compounds $\{dmit(Mes)\}_2$, $\{dmit(Trip)\}_2$, $\{dbt(Mes)_2\}$ and $\{tbt(Mes)_2\}$ as a consequence of S,C- and S,S-coupling processes. In the case of [$Ni(Mes)(dmitMes)(PPh_2Me)$], $\{dmit(Trip)\}_2$, [$Ni_3(bdt)_3$-$(PPh_2Me)_2$] and [$Ni(bdtMes)_2$] the X-ray analyses are also presented to confirm the proposed structures.

Introduction

Tin(IV) complexes are commonly used as transmetallating agents for a wide variety of anions,[1] due to the advantages of solubility in conventional organic solvents and of producing easily removable (by washing) tin(IV) halide compounds as by-products. Organometallic tin complexes have been employed in transmetallation reactions with group 13 metallic salts for the preparation of group 13 polyfunctional Lewis acids:[2–5] with RLi to prepare organolithium complexes[6] for structural and spectroscopic studies; with transition metal halides to provide a new route to metallocene derivatives;[7–12] with germanium halides[13] to give Ge-based reagents for organic synthesis and in the synthesis of lanthanoid complexes by redox transmetallation reactions.[14,15] Organotin(IV) derivatives containing thiolate or selenolate or the hybrid phosphine–thiolate ligands have been shown to be good ligand transfer reagents to metals of groups 7–10. Thus, iron(IV)[16] and ruthenium(IV),[16,17] rhodium(I) and iridium(I),[18] nickel(II), palladium(II) and platinum(II),[19–22] gold(I)[23–26] and gold(III)[27,28] complexes have been prepared in very mild conditions. In addition, processes involving transmetallation reactions as key steps for a catalytic process have recently been of considerable interest,[29,30] particularly the Stille reaction in the formation of C–C bonds, which uses organometallic tin complexes as starting materials and it is believed to proceed *via* a cycle of oxidative addition–transmetallation–reductive elimination,[31–33] where the transmetallation process is the rate-determining step.[31–35] Another interesting process is the rhodium-catalyzed addition of organometallic reagents to carbon–heteroatom,[36,37] reactions which commonly involve organorhodium complexes as active species generated by transmetallation with organometallic reagents such as tin.[38–42]

In the particular case of dithiolate tin(IV) derivatives we have shown that in the use of such derivatives as transmetallating agents with nickel complexes, the reaction does not proceed in the expected way of a simple dithiolate ligand transfer. Therefore, we have described in a preliminary communication[19] that using the organometallic nickel(II) derivative, [$NiBr(Mes)(PPh_2Me)_2$] (Mes = mesitylene), in the presence of [$SnMe_2(dmit)$] (dmit = 4,5-dimercapto-1,3-dithiole-2-thione), a mixture of products are obtained instead of the expected [$Ni_2(\mu\text{-dmit})Br_2(Mes)_2(PPh_2Me)_4$]. Here we extend this reaction to the similar nickel derivatives: [$NiBrR'(PR_3)_2$] (R' = Mes, Trip (2,4,6-tri-isopropylphenyl), PR_3 = PPh_3, PPh_2Me), using dmit, bdt (1,2-benzenedithiolate) and tdt (3,4-toluenedithiolate) as dithiolate ligands. This gives rise to a mixture of products, some of them as a result of S,C- and S,S-coupling processes.

Results and discussion

The reaction of [$SnMe_2(dmit)$] with [$NiBr(Mes)(PR_3)_2$] (PR_3 = PPh_3 and PPh_2Me) (Scheme 1) in 1 : 1 or 1 : 2 molar ratios at room temperature in acetone gave a mixture of products which was separated by chromatography and identified spectroscopically. Since the same complexes are obtained with both stoichiometries and an excess of the nickel starting material was detected in the 1 : 2 ratio, we performed all the reactions in the 1 : 1 ratio. Apart from $\{dmitMes\}_2$, which was previously described by X-ray studies in a preliminary communication,[19] we have obtained [$Ni(dmit)(PR_3)]_2$ and [$Ni(Mes)(dmitMes)(PR_3)$] as pure samples.

The [$Ni(dmit)(PR_3)]_2$ (PR_3 = PPh_3, **1**; PPh_2Me, **2**) compounds show a singlet in the $^{31}P\{^1H\}$ NMR spectra and only the corresponding phosphine signals in the ^1H NMR spectrum. The elemental analysis indicate the stoichiometry of [$Ni(dmit)(PR_3)]_n$. The lack of ionisation in the liquid secondary ion mass spectrometry (LSIMS) spectra in the case of **1** and the poor solubility of both of them for a cryoscopic molecular weight measurement precludes the obtaining of any meaningful information about the value of *n*. We can postulate the structure of these compounds as dimers in comparison with the similar dithiolate (bdt, tdt) derivatives that will be depicted later on, although a polynuclear structure is not excluded. Though the structure of the isolated

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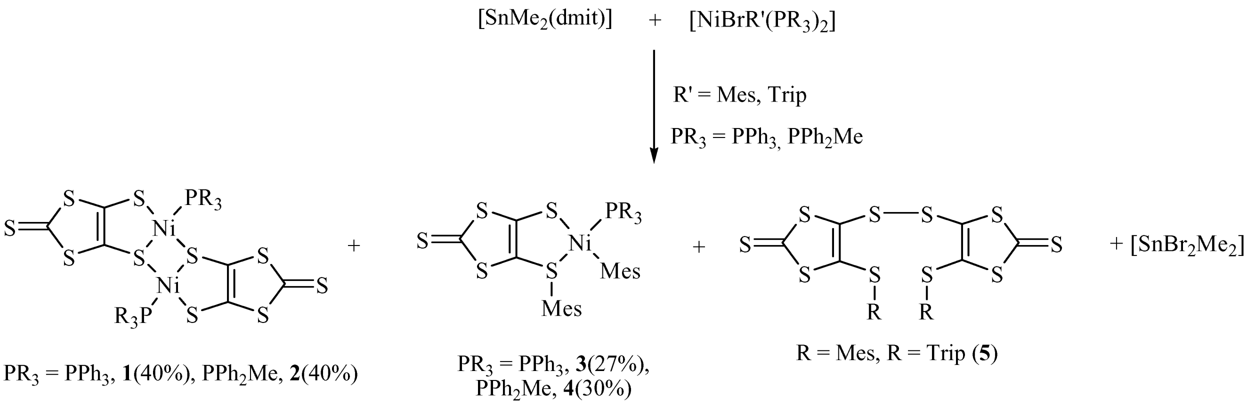


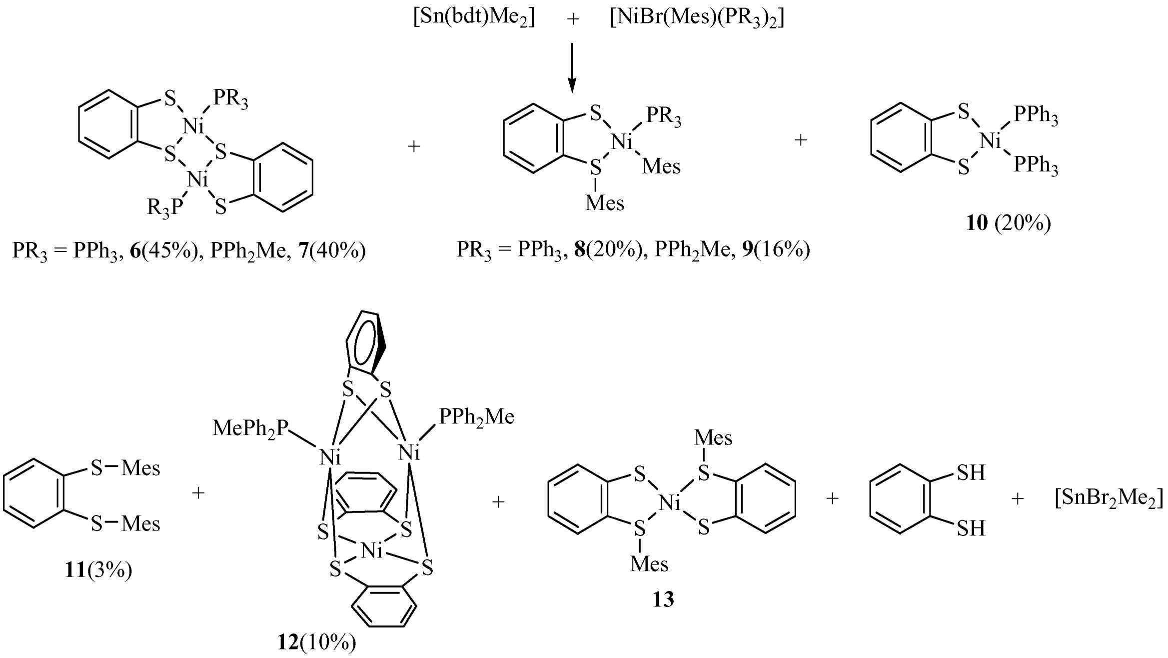
Scheme 1 Reaction of [SnMe$_2$(dmit)] with [NiBr(Mes)(PR$_3$)$_2$] (PR$_3$ = PPh$_3$ and PPh$_2$Me) with the yields in brackets.

compounds, when comparing the two different phosphines, should be similar, the order of elution in the chromatographic separation process was different depending on the PR$_3$ used. So, as is described in the experimental, compound **1** is obtained first and **2** is obtained last. [Ni(Mes)(dmitMes)(PR$_3$)] (PR$_3$ = PPh$_3$, **3**; PPh$_2$Me, **4**) were isolated as mixtures of two isomers in an 8 : 1 amount (data obtained from ^{31}P{^{1}H} NMR spectra). The existence of the isomers arises from the relative position of the phosphine, either *trans* to the thiolate or *trans* to the thioether group. Recrystallization of the mixture in the case of PR$_3$ = PPh$_3$ in dichloromethane, gave an homogeneous sample of yellow crystals. The X-ray analysis of one of them (*vide infra*) revealed the *trans* position of the triphenylphosphine with respect to the thioether group. The crystals exist as the major isomer (**3a**), with the phosphine molecule *trans* to the thioether group, as deduced by ^{31}P{^{1}H}NMR, and the minor isomer (**3b**), with the phosphine molecule *trans* to the thiolate group. We assume that the structures of **3a** and **4a** should be similar.

When using a bulkier radical, such as 2,4,6-trisisopropylphenyl (Trip), instead of Mes in the starting nickel complex, [NiBr(Ar)(PPh$_3$)$_2$], the formation of a product analogous to {dmit(Mes)}$_2$ ({dmit(Trip)}$_2$, **5**) occurs, but as the major product of the reaction. Although [Ni(dmit)(PPh$_3$)]$_2$ (**1**) is obtained as well, the related thiolate thioether derivative (**3**) [Ni(Trip)(dmitTrip)(PPh$_3$)] is not, probably as a consequence of steric factors.

The same reaction using [NiBr(Mes)(PR$_3$)$_2$] was performed with two different dithiolates: bdt (1,2-benzenedithiolate) and tdt (3,4-toluenedithiolate). Using [SnMe$_2$(bdt)] as starting material, the reaction gave again a mixture of products (Scheme 2), which were all identified and characterized spectroscopically.

In this case, in addition to the similar dmit derivatives [Ni(bdt)(PR$_3$)]$_2$ (PR$_3$ = PPh$_3$, **6**; PPh$_2$Me, **7**) and [Ni(Mes)(bdtMes)(PR$_3$)] (PR$_3$ = PPh$_3$, **8**; PPh$_2$Me, **9**), [Ni(bdt)(PR$_3$)$_2$] (PR$_3$ = PPh$_3$, **10**), {bdt(Mes)$_2$} (**11**), [Ni$_3$(bdt)$_3$(PPh$_2$Me)$_2$] (**12**) and [Ni(bdtMes)$_2$] (**13**) were isolated. The last



Scheme 2 Reaction of [NiBr(Mes)(PR$_3$)$_2$] with [Sn(bdt)Me$_2$] with the yields in brackets.

two derivatives have also been structurally characterised by X-ray analysis.

The ^{1}H NMR spectra of $[Ni(dbt)(PR_3)]_2$ (PR_3 = PPh_3, **6**; PPh_2Me, **7**) show the bdt protons displaced from the phosphine signals to higher fields, which permits a complete assignment of the resonances by ^{1}H,^{1}H-COSY experiments. The LSIMS+ (nba as matrix) spectra show that, in both cases, the molecular peak (considering the compounds as dimers) and the cryoscopic molecular weight measurement in chloroform (see experimental) are in agreement with a dinuclear structure. The isolation of such products is different depending on the phosphine. Complexes **6** and **8** were isolated by precipitation, due to their lower solubilities. However, for **11**, **12** and **13**, where PR_3 = PPh_2Me, a chromatographic separation of the mixture is obligatory for their isolation. $[Ni(Mes)(bdtMes)(PR_3)]$ (PR_3 = PPh_3, **8**; PPh_2Me, **9**) were again obtained as a 7 : 1 mixture of isomers (PR_3 *cis* or *trans* to the thioether group). We could imagine a similar structure to that described for **3a** for the major isomer. In the case of complex **8a** (the most abundant isomer), the *trans* disposition of the phosphine to the thioester group could be determined by a NOE experiment. The intensities of the signals due to the protons of PPh_3 only changed when the *o*-Me proton signal, at δ 2.06 ppm, of the mesitylene bonded to the nickel centre was irradiated, and remained unchanged when the *o*-methyl protons of the mesitylene radical bonded to the S atom (δ 1.94 ppm) were irradiated. The ^{1}H,^{1}H-NOESY spectrum confirms that the major isomer is the one with PPh_3 *trans* to the thioether.

The rest of the identified complexes were: $[Ni(bdt)(PR_3)_2]$ (only obtained in the case of PR_3 = PPh_3, **10**), $[(bdt)(Mes)_2]$ (**11**), $[Ni_3(bdt)_3(PPh_2Me)_2]$ (**12**) and $[Ni(bdtMes)_2]$ (**13**). Using the phosphine PPh_2Me, a trinuclear nickel(II) derivative with the formula $[Ni_3(bdt)_3(PPh_2Me)_2]$ (**12**) is obtained, instead of the related mononuclear $[Ni(bdt)(PR_3)_2]$, obtained when using PPh_3. A similar trinuclear derivative with the phosphine PPh_3 was previously obtained as the major product by Kovacs *et al.*[43] in the reaction of a solution of Na_2bdt in THF with $[NiCl_2(PPh_3)_2]$ in a 1 : 1 molar ratio. In the ^{1}H NMR spectrum of $[Ni_3(bdt)_3(PPh_2Me)_2]$ (**12**), the bdt signals are displaced to higher fields than the phosphine protons, as seen in the dinuclear derivatives, making the corresponding assignment much easier. The LSIMS+ spectrum displays the molecular peak and the peaks corresponding to the successive loss of the phosphine molecules. In both reactions $\{bdt(Mes)_2\}$ (**11**) can be identified. In this case the homologue of $\{dmitR\}_2$ (R = Mes or Trip), as a result of a S,S- and S,C-coupling, is not obtained; instead only a S,C-coupling is achieved in **11**.

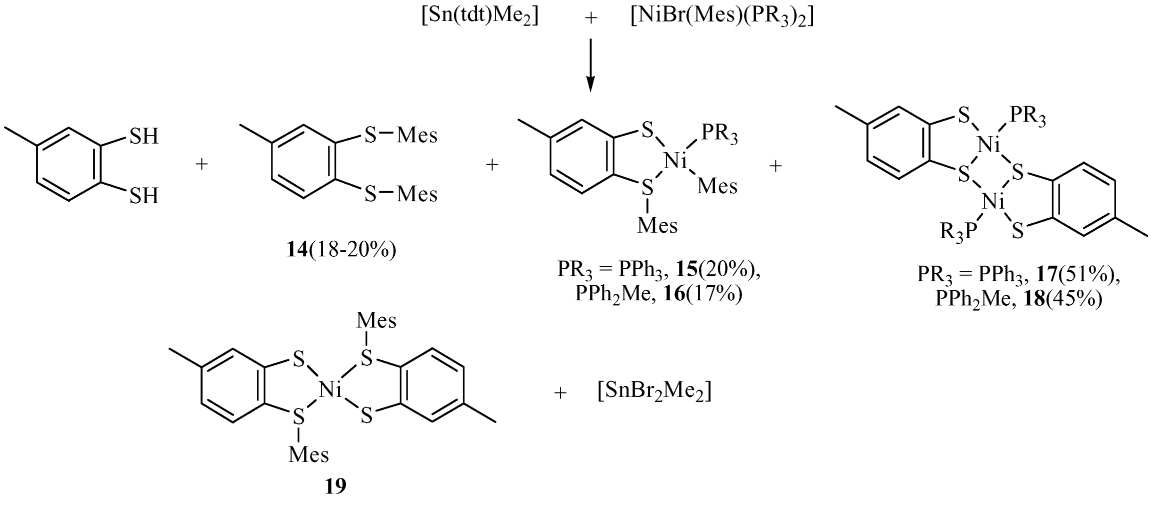
The yield of the isolated bdt-complexes is different depending on the reaction conditions, such as if the experiment is performed at room temperature or refluxed. The dinuclear derivatives are obtained in slightly higher yields when the reaction is carried out under reflux.

During the isolation of $[Ni(bdt)(PPh_2Me)]_2$ (**7**), a very small amount of an additional compound could be detected in the ^{1}H NMR spectrum. This compound was identified as $[Ni(bdtMes)_2]$ (**13**), as deduced by NMR and X-ray analysis. Although a better separation between **7** and **13** by column chromatography was not possible, a recrystallisation of the sample gave red microcrystals corresponding to compound **13**, accompanied by opaque black crystals, which were not of diffraction quality.

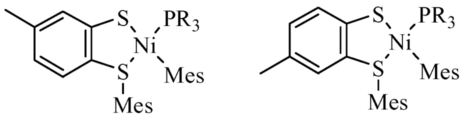
When using 3,4-toluenedithiolate (tdt) as the dithiolate ligand, the complexes are obtained in the same order of elution, regardless of the phosphine used (Scheme 3). Apart from 3,4-toluenedithiole, $\{tdt(Mes)_2\}$ (**14**), $[Ni(Mes)(tdtMes)(PR_3)]$ (PR_3 = PPh_3, **15**; PPh_2Me, **16**), $[Ni(tdt)(PR_3)]_2$ (PR_3 = PPh_3, **17**; PPh_2Me, **18**) and $[Ni(tdtMes)_2]$ (**19**) were separated by column chromatography.

Compound **14** was identified by ^{1}H NMR, displaying the presence of two different mesitylene groups, and LSIMS+ (nba as matrix), with the presence of the molecular peak as the parent peak.

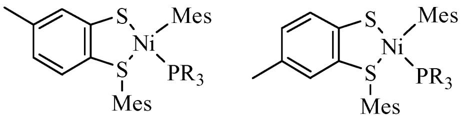
$[Ni(Mes)(tdtMes)(PR_3)]$ (PR_3= PPh_3, **15**; PPh_2Me, **16**) were each isolated as a mixture of 4 isomers, which are a consequence of the relative position of the Me group in the tdt dithiolate ligand and the *cis* or *trans* disposition of the phosphine, with two isomers being the majority in a relation close to 7 : 1. In this case, we distinguished the two majority isomers as one with the Me group in the *meta* position to the thiolate and the other with the Me *meta* to the thioether group (Fig. 1), but we have no evidence regarding their structure, although we can make propositions, comparing



Scheme 3 Reaction of $[NiBr(Mes)(PR_3)_2]$ with $[Sn(tdt)Me_2]$ with the corresponding yields in brackets.



Majority isomers (a, b)

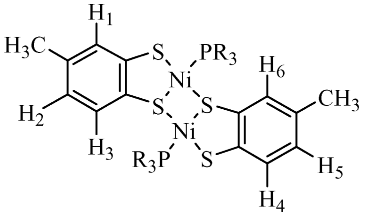


Minority isomers (c, d)

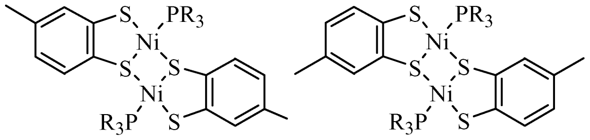
Fig. 1 Different isomers for the mononuclear thiolate–thioether nickel derivative with tdt as the dithiolate ligand.

them to the above described for dmit and bdt dithiolates, with the phosphine *trans* to the thioether group.

A new blend of isomers is identified for [Ni(tdt)(PR$_3$)]$_2$ (PR$_3$ = PPh$_3$, **17**; PPh$_2$Me, **18**): two symmetric isomers and one non-symmetric (Fig. 2). The presence of these three isomers was confirmed by a ^{31}P{^{1}H}-^{31}P{^{1}H} COSY experiment. The symmetric species appear as singlets whereas the asymmetric isomer appears as an AB system. Only in the case of **17** are those signals detected in a room temperature NMR experiment. However, in the case of **18** (PR$_3$ = PPh$_2$Me) there is an unique signal at 20 °C, which is resolved at −60 °C to give the same pattern as the one observed in **17**. We describe these complexes as dimers of their bdt homologues, on the basis of their mass spectra and their cryoscopic molecular weight measurement. These dinuclear complexes are again obtained in slightly higher yields when the reaction is performed under reflux.



Non symmetric isomer (a)



Symmetric isomers (b and c)

Fig. 2 Different isomers for the dinuclear nickel derivative with tdt as the dithiolate ligand.

As in the reaction with bdt as dithiolate ligand, a similar derivative to [Ni(bdtMes)$_2$] (**13**), [Ni(tdtMes)$_2$] (**19**), is detected in very small amounts in the isolation of the dimeric compounds. The ^{1}H NMR spectrum displays a symmetric disposition of the Me group in the tdtMes ligand, giving only one signal for both Me and Mes groups. However, with this dithiolate, neither higher nuclearities nor the homologue of the [Ni(SS)(PPh$_3$)$_2$] complex are observed during the reaction.

X-Ray structures

Structure of [Ni(Mes)(dmitMes)(PPh$_3$)] (3a). The molecule (Fig. 3) consists of a mononuclear nickel(II) centre with a triphenylphoshine, a mesitylene group and a mixed dmit ligand with thiolate and thioether groups, all coordinated to the metallic centre. The coordination around the nickel can be considered as a distorted square-planar geometry. The main distortion comes from the S(1)–Ni(1)–C(13) and S(1)–Ni(1)–P(1) angles which are 84.73(8)° and 170.29(3)° respectively. The mesitylene group bonded directly to the nickel centre is in a nearly perpendicular disposition with respect to the NiS$_2$CP plane (torsion angle of about 94°). It is worth noting that the Ni–S(thioether) distance of 2.1997(8) Å is shorter than the respective Ni–S(thiolate) bond length (2.2308(9) Å) in [Ni(Et$_2$NS$_2$–H)$_2$] (Et$_2$NS$_2$–H = *N*,*N*-diethyl-2-(2-mercaptothiophenyl)ethylamine),[44] [Ni(SSR)$_2$] (SSR = bsms—4-mercapto-3,3-methyl-1-phenyl-2-thiabutane[45]—and 2-ethoxycarbonylsulfanyl-1,2-bis(methylthio)-1-ethenethiolato)[46] and in sulfur rich nickel complexes with a bis(2-mercaptophenyl)sulfide ligand.[47,48] Ni–S(thioether) distances in comparable complexes are usually in the range of 2.17–2.18 Å[49,50] and Ni–S distances in nickel thioether–thiolate complexes frequently do not differ at all,[51] but in this case, the presence of the longer Ni–thiolate distance is in accordance with the higher *trans* influence of the mesitylene group.[52] There are only two examples in the literature, as confirmed by a search of dmit–thiolate–thioether nickel complexes described by X-ray analysis in the Cambridge Crystallographic Data Base: [Ni(dmit–Me)$_2$(dppe)][53] and [Ni(dmit-*o*-CH$_2$C$_6$H$_4$CH$_2$-dmit)(py)$_2$].[25] However, in both structures the Ni–S(thioether) distances are greater than the respective Ni–S(thiolate) bond lengths, precisely the opposite effect to what we have observed in **3a**. The remaining Ni–P (2.1761(8) Å) and Ni–C (1.934(3) Å) bond lengths are similar to those found in related organometallic phosphino-thiolate derivatives.[54–58] The distances in the dmit ligand [S4–C3 1.637(3), C1–C2 1.334(4), C2–S2 1.743(3) and

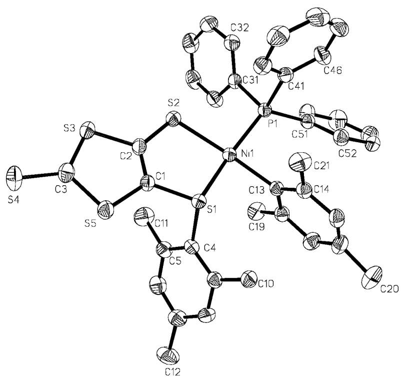


Fig. 3 Molecular structure of complex **3a**. Selected bond lengths [Å] and angles [°]: Ni(1)–C(13) 1.934(3), Ni(1)–P(1) 2.1761(8), Ni(1)–S(1) 2.1997(8), Ni(1)–S(2) 2.2308(8), S(1)–C(1) 1.759(3); C(13)–Ni(1)–P(1) 90.86(9), C(13)–Ni(1)–S(1) 84.73(8), P(1)–Ni(1)–S(1) 170.29(3), C(13)–Ni(1)–S(2) 176.70(9), P(1)–Ni(1)–S(2) 92.41(3), S(1)–Ni(1)–S(2) 91.96(3). H omitted for clarity.

C1–S1 1.759(3) Å] are similar to those found in metallic complexes with the dmit ligand acting as a thiolate–thioether ligand.[25,53,59,60]

Structure of {dmit(Trip)$_2$} (5). Compound **5** gave single crystals suitable for X-ray structure analysis. The molecular structure (Fig. 4) confirms the presence of two (dmit)Trip units interconnected through a S–S bond of 2.082(2) Å. As stated above, a similar structure, previously reported by us,[19] with a Mes group, had a S–S bond length of 2.096(3) Å. The main difference between them consists of the disposition of the two C_3S_5 (dmit) units. In compound **5**, both rings are orientated on the same side of the molecule whereas in the other, the dmit subunits have opposite orientations, probably due to the formation of dimers in the crystal packing (see below). These dmit units are in a nearly parallel disposition with a dihedral angle of 5.99°; however the Trip rings are both bent, with an angle of about 17.2°. The C–S (1.74 Å on average) and the C=C (1.345(7) and 1.354(7) Å) distances in the dmit skeleton are similar to those found in dmit derivatives such as {dmit(Mes)$_2$},[19] C_3S_8,[61] C_6S_{10},[62] $(NMe_4)_2C_6S_{10}$,[63] C_6S_{12},[64–66] C_6S_{14},[66] [FeCp(CO)$_2$(C_6S_{10})][67] and $(PPh_4)_2C_{12}S_{16}$.[63] The stacking of the molecules along the direction perpendicular to the (100) plane presents intermolecular S···S contacts of 3.41 Å (shorter than the sum of the van der Waals radii—3.7 Å), giving the formation of dimers (Fig. 5).

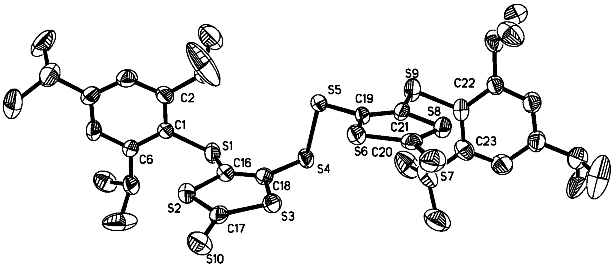


Fig. 4 Molecular structure of complex **5**. Selected bond lengths [Å] and angles [°]: S(1)–C(16) 1.752(6), S(1)–C(1) 1.789(6), S(4)–C(18) 1.750(6), S(4)–S(5) 2.083(2), S(5)–C(19) 1.767(6), C(19)–C(21) 1.354(7), S(7)–C(20) 1.632(6); C(16)–S(1)–C(1) 99.2(3), C(21)–S(9)–C(22) 100.3(3), C(2)–C(1)–S(1) 118.7(4), S(3)–C(18)–S(4) 119.6(3), S(6)–C(19)–S(5) 120.1(3), C(19)–C(21)–S(9) 124.3(5). H omitted for clarity.

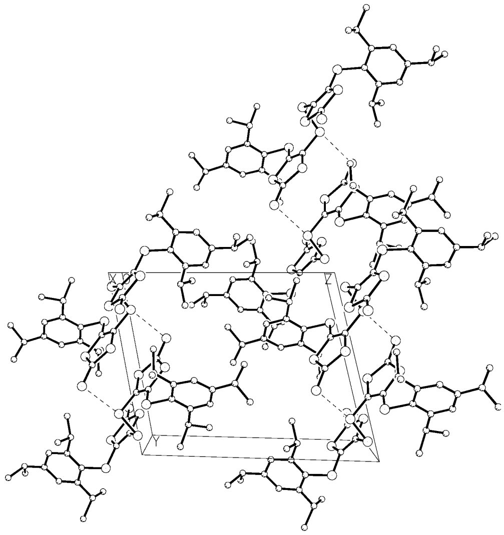


Fig. 5 Stacking of compound **5** molecules along the direction perpendicular to the (100) plane.

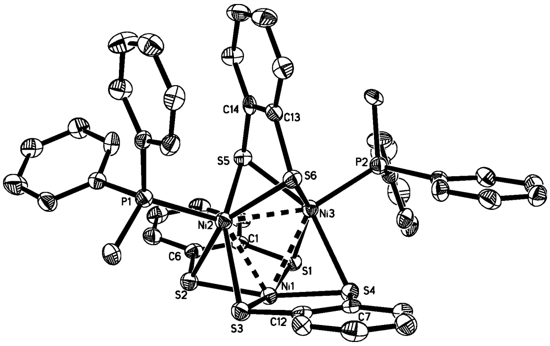


Fig. 6 Molecular structure of complex **12**. Selected bond lengths [Å]: Ni(1)–S(2) 2.1731(14), Ni(1)–S(3) 2.1742(15), Ni(1)–S(4) 2.1748(14), Ni(1)–S(1) 2.1753(15), Ni(1)–Ni(2) 2.5104(10), Ni(1)–Ni(3) 2.5262(9), Ni(2)–P(1) 2.2410(14), Ni(2)–S(6) 2.2994(14), Ni(2)–S(5) 2.3443(15), Ni(2)–S(2) 2.4113(14), Ni(2)–S(3) 2.4692(14), Ni(2)–Ni(3) 2.4729(10), Ni(3)–P(2) 2.2250(15), Ni(3)–S(5) 2.2917(14), Ni(3)–S(6) 2.3066(14), Ni(3)–S(4) 2.4411(14), Ni(3)–S(1) 2.4732(14). H omitted for clarity.

Structure of [Ni$_3$(bdt)$_3$(PPh$_2$Me)$_2$] (12). Dark brown crystals of complex **12** were grown from a dichloromethane solution and the resulting X-ray crystal structure is shown in Fig. 6. The structure is similar to the previously described trinuclear cluster [Ni$_3$(bdt)$_3$(PPh$_3$)$_2$],[43] with a cyclic trigonal prismatic Ni_3S_6 core. In both cases the intermetallic Ni···Ni separations are shorter than other Ni-thiolate clusters (distances range from 2.633 to 3.131 Å),[68–74] ranging from 2.500 to 2.549 Å in the case of PPh$_3$ and from 2.5104 to 2.5462 Å in complex **12**, which are close to the distance of 2.49 Å in the metal.[75] Two of the nickel atoms are five coordinated while the other displays a highly distorted square-planar coordination to two benzenedithiolate ligands, with angles S(4)–Ni(1)–S(2) 166.63(6), S(1)–Ni(1)–S(3) 164.91(6), S(1)–Ni(1)–S(2) 92.95(5) and S(2)–Ni(1)–S(3) 84.79(5)° and a deviation of the nickel centre from the plane of 0.2152(7) Å. The dihedral angles between the S(1)–S(2)–S(3)–S(4) plane and the phenyl rings C(1)–C(2)–C(3)–C(4)–C(5)–C(6) and C(7)–C(8)–C(9)–C(10)–C(11)–C(12) are 7.07 and 12.07°, respectively, which reinforces the geometrical distortion from planarity of the Ni(bdt)$_2$ unit. The remaining two nickel atoms, Ni(2) and Ni(3), show a distorted square pyramidal coordination lying 0.4438(7) and 0.4440(7) Å, respectively, above the corresponding S_4 basal plane. These displacements are smaller than those observed (0.579(1) and 0.587 Å) in the equivalent structure with PPh$_3$ ligands. The *cis* and *trans* S–Ni–S angles in the basal plane of the square pyramid range from 73.8(5) to 98.82(5) and 150.84(5) to 151.32(5)°, respectively and the P–Ni–S angles range from 95.73(5) to 109.13(5)°. The Ni–S bond lengths in the dianion [Ni(dbt)$_2$]$^{2-}$ (2.1743 Å on average) are shorter than the distances observed with the bridging bdt units (on average: Ni(2)–S 2.381 Å and Ni(3)–S 2.3782 Å) as in the cluster with PPh$_3$ ligands. Both Ni(2) and Ni(3) are bonded to one phosphine molecule (PPh$_2$Me) in the apical position of the pyramid with typical distances Ni–P of 2.2410(14) and 2.2250(15) Å, respectively.

Structure of [Ni(bdtMes)$_2$] (13). The molecule structure of complex **13** is shown in Fig. 7. It is an homoleptic nickel(II) complex with two bdtMes ligands (bdtMes = *o*-(mesitylenethio)-thiophenolate-S,S′) exhibiting crystallographic centrosymmetry and planar [NiS$_4$] cores. The NiS$_4$ unit, including the phenyl rings, is highly distorted from planarity. The dihedral angles between the NiS$_4$ core and the phenyl rings are 64.1 and 69.7° and the nickel atom is 1.4362(25) Å out of the plane. The two mesitylene radicals are nearly perpendicular to the Ni(dbt)$_2$ unit, with a torsional angle of 80.9°. In this molecule the two Ni–S distances are different, with the Ni–S(thiolate) (2.1928(19)Å) bond longer than the Ni–S(thioether) (2.150(15) Å) bond, as observed in **3**. However, similar Ni–thiolate–thioether homoleptic derivatives display close distances for both units[76,77] or longer distances for the Ni–thioether unit.[46,78] The discrete molecules show a stacking along the direction perpendicular to the (100) plane, with a Ni···Ni separation of 9.966 Å (Fig. 8).

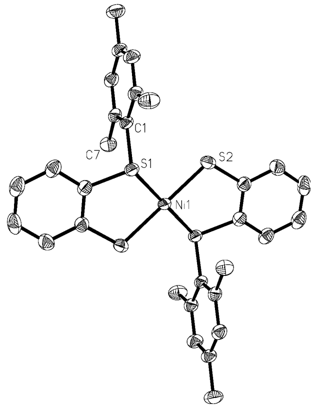


Fig. 7 Molecular structure of complex **13**. Selected bond lengths [Å] and angles [°] (#1: −*x*, −*y*, −*z*): Ni(1)–S(1) 2.150(15), Ni(1)–S(2) 2.1927(19), S(1)–C(1) 1.778(17), S(1)–Ni(1)–S(1)#1: 180.0, S(1)–Ni(1)–S(2) 90.29(12), S(1)#1–Ni(1)–S(2) 89.71(12), S(1)–Ni(1)–S(2)#1 89.71(12). H omitted for clarity.

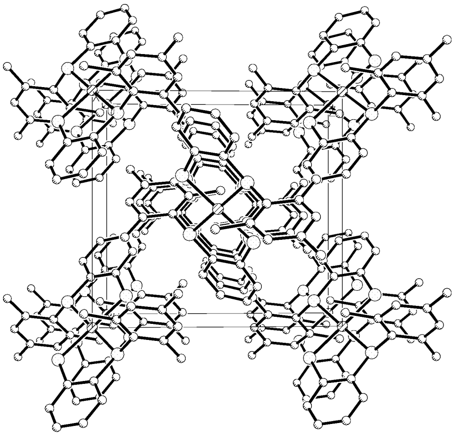


Fig. 8 Stacking of compound **13** molecules along the direction perpendicular to the (100) plane.

The progress of the transmetallation reactions were monitored by the use of NMR techniques, in particular by ^{1}H NMR, ^{31}P{^{1}H}NMR and ^{119}Sn NMR, in order to determine a possible mechanism.

In the reactions with dmit as the dithiolate ligand, the first new product detected is the one resulting from the C,S and S,S-coupling, {dmitR}$_2$ (R = Mes, Trip, **5**), whose signals appear within the first 5 min of reaction and remain unchanged throughout the course of the reaction. The signals of the starting nickel complexes, [NiBr(Mes)(PR$_3$)$_2$] (PR$_3$ = PPh$_3$ and PPh$_2$Me), decrease at the same time that the ones corresponding to the new nickel compounds, [Ni(Mes)(dmitMes)(PR$_3$)] and [Ni(dmit)(PR$_3$)]$_2$, increase.

In all the reactions, free PR$_3$ is detected in the ^{31}P{^{1}H} NMR measurements, in addition to some new resonances during the first minutes of the reaction that then disappear rapidly, which are probably due to intermediate species. [SnBr$_2$Me$_2$] is also identified in the ^{1}H NMR and^{119}Sn NMR spectra during the course of the reaction, in addition to some signals from unidentified tin complexes.

We presume that the formation of {dmitR′}$_2$ (R′ = Mes, Trip, **5**) and [(S–S)(Mes)$_2$] [S–S = bdt (**12**), tdt (**14**)] should go by different pathways, since {(S–S)(Mes)$_2$} can be detected by heating [Ni(Mes)(S–SMes)(PR$_3$)] [S–S = bdt (**8**, **9**), tdt (**15**, **16**)] in acetone, whereas [Ni(Mes)(dmitMes)(PR$_3$)] (**3**, **4**) remain unaltered under the same conditions.

Although it was neither possible to isolate nor to characterize any intermediates by NMR, we suggest a possible mechanism (Scheme 4) based on the obtained complexes. We think that the formation of a heteronuclear intermediate ***a*** should be the first step. ***a*** could then evolve to the intermediates ***b*** and/or ***c*** as a consequence of a selective cleavage of the S–Ni or S–Sn bonds, which, for the formation of ***b***, is accompanied by a mesitylene group shift from the metal centre to the sulfur atom. Such intermediates then proceed to the described derivatives according to Scheme 4

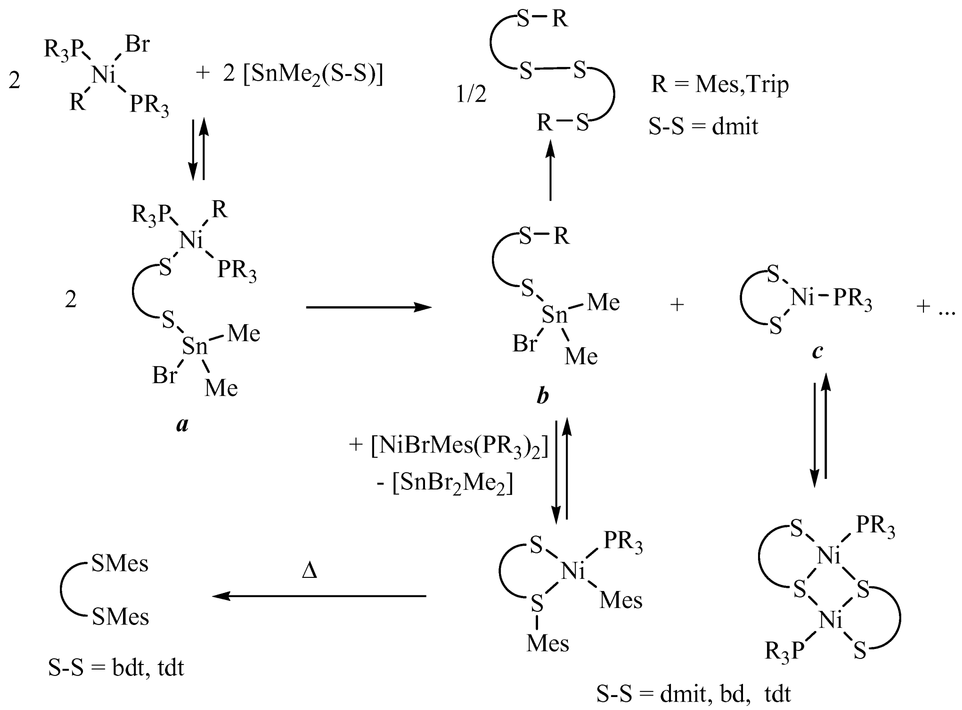
Experimental

General data

The C, H, N and S analyses were measured on a Perkin-Elmer 2400 microanalyser. The infrared spectra were recorded on a Perkin-Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on a Varian UNITY 300, BRUKER ARX 300 or AV400 spectrometer, in CDCl$_3$ or (CD$_3$)$_2$CO at room temperature, if not otherwise mentioned (300 MHz for ^{1}H and 121,4 MHz for ^{31}P). Chemical shifts are cited relative to SiMe$_4$ (^{1}H) and 85% H$_3$PO$_4$ (external, ^{31}P). Mass spectra were recorded by liquid secondary ion mass spectrometry (LSIMS+) on a VG Autospec, using nba (nitrobenzylalcohol) as matrix and a cesium gun.

Materials

The starting materials, [SnMe$_2$(S-S)],[28] [NiBr(Trip)L$_2$] and [NiBr(Mes)L$_2$],[79] were prepared by published procedures. In the case of [NiBr(Trip)L$_2$] the preparation is similar to that reported for [NiBr(Mes)L$_2$], but using Mg(Trip)Br instead of Mg(Mes)Br. All other reagents were commercially available and were used as supplied.



Scheme 4 Proposal of the mechanism of the dithiolate transfer reaction.

Reaction of [SnMe$_2$(dmit)] with [NiBr(Mes)(PPh$_3$)$_2$]

To a stirred solution of [SnMe$_2$(dmit)] (0.103 g, 0.3 mmol) in acetone (20 ml) was added [NiBr(Mes)(PPh$_3$)$_2$] (0.235 g, 0.3 mmol). After 5 h of stirring, a brown solid precipitated and was identified as [Ni(dmit)(PPh$_3$)]$_2$ (**1**). The solid was filtered off and after evaporation of the solvent under reduced pressure the residue was chromatographed on silica gel using dichloromethane–hexane (1 : 3) as the eluent to give, in order of elution: {dmitMes}$_2$ [19] and [Ni(Mes)(dmitMes)(PPh$_3$)] (**3**).

[Ni(dmit)(PPh$_3$)]$_2$ (**1**), brown solid. Yield: 40% (based on nickel). Anal. calcd for $C_{42}H_{30}Ni_2P_2S_{10}$: C, 48.76; H, 2.92; S, 30.99. Found: C, 48.50; H, 2.83; S, 31.06. Mp (°C): 173, IR: ν(C=S) 1056, 1050, 1026 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.20–8.00 (m, 30H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 30.3 (s).

[Ni(Mes)(dmitMes)(PPh$_3$)] (**3**), yellow solid. Yield: 27% (based on nickel). Anal. calcd for $C_{39}H_{37}NiPS_5$: C, 61.98; H, 4.93; S, 21.21. Found: C, 61.84; H, 4.81; S, 21.48. Mp (°C): 180. IR: ν(Mes) 1600, 848 cm^{-1}; ν(C=S) 1057, 1011 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.00 (s, 3H, *p*-Me (Mes)), 2.09 (s, 12H, *o*-Me (Mes)), 2.18 (s, 3H, *p*-Me (Mes)), 6.05 (s, 2H, *m*-H (Mes)), 7.23 (s, 2H, *m*-H (Mes)), 7.10–7.50 (m, 12H, PPh$_3$), 7.60–7.80 (m, 3H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 26.9 (s) (isomer a), 21.6 (s) (isomer b). MS (LSIMS+): m/z (%) = 754 (90) [M]$^+$.

Reaction of [SnMe$_2$(dmit)] with [NiBr(Mes)(PPh$_2$Me)$_2$]. To a stirred solution of [SnMe$_2$(dmit)] (0.103 g, 0.3 mmol) in acetone (20 ml) was added [NiBr(Mes)(PPh$_2$Me)$_2$] (0.197 g, 0.3 mmol). After 5 h of stirring the solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel using dichloromethane–hexane (1 : 3) as the eluent to give, in order of elution: {dmitMes}$_2$,[19] [Ni(Mes)(dmitMes)(PPh$_2$Me)] (**4**) and [Ni(dmit)(PPh$_2$Me)]$_2$ (**2**).

[Ni(Mes)(dmitMes)(PPh$_2$Me)] (**4**), yellow solid. Yield: 30% (based on nickel). Anal. calcd for $C_{34}H_{35}NiPS_5$: C, 58.87; H, 5.08; S, 23.11. Found: C, 58.70; H, 5.33; S, 23.51. Mp (°C): 180. IR: ν(Mes) 1600, 849 cm^{-1}; ν(C=S) 1064, 1034 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.01 (d, 3H, J = 9.9 Hz, PPh$_2$*Me*), 2.03 (s, 3H, *p*-Me (Mes)), 2.06 (s, 3H, *p*-Me (Mes)), 2.16 (s, 6H, *o*-Me (Mes)), 2.18 (s, 6H, *o*-Me (Mes)), 6.28 (s, 2H, *m*-H (Mes)), 6.69 (s, 2H, *m*-H (Mes)), 7.37–7.69 (m, 10H, P*Ph$_2$*Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 11.6 (s) (isomer a), 14.7 (s) (isomer b). MS (LSIMS+): m/z (%)= 692 (28) [M]$^{+\bullet}$.

[Ni(dmit)(PPh$_2$Me)]$_2$ (**2**), brown solid. Yield: 40% (based on nickel) Anal. calcd for $C_{32}H_{26}Ni_2P_2S_{10}$: C, 42.21; H, 2.88; S, 35.22. Found: C, 42.44; H, 2.65; S, 35.05. Mp (°C): 180. IR: ν(C=S) 1061, 1028 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.24 (d, 6H, J = 12.6 Hz, PPh$_2$*Me*), 7.44–7.46 (m, 12H, P*Ph$_2$*Me), 7.76–7.83 (m, 8H, P*Ph$_2$*Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 36.3 (s). MS (LSIMS+): m/z (%) = 455 (92) [M – dmit – Ni – PPh$_2$Me]$^+$.

Reaction of [SnMe$_2$(dmit)] with [NiBr(Trip)(PPh$_3$)$_2$]. This reaction was carried out in a similar way to the first reaction, described with [NiBr(Mes)(PPh$_3$)$_2$], but starting with [NiBr(Trip)(PPh$_3$)] (0.260 g, 0.3 mmol). A brown solid, identified as [Ni(dmit)(PPh$_3$)]$_2$ (**1**) precipitated after 5 h of stirring (yield 40%, based on nickel). The solid was filtered off and, after evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel using dichloromethane–hexane (1 : 3) as the eluent to give {dmitTrip}$_2$ (**5**) as the main product.

{dmitTrip}$_2$ (**5**), yellow solid. Yield: 50% (based on dmit). Anal. calcd for $C_{36}H_{46}S_{10}$: C, 54.21; H, 5.80; S, 40.11. Found: C, 54.09; H, 5.64; S, 40.38. Mp (°C): 150. IR: ν(C=S) 1074, 1016 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.22 (d, 12H, J = 6.9 Hz, *p*-CH*Me$_2$* (Trip)), 1.24 (d, 24H, J = 6.9 Hz, *o*-CH*Me$_2$* (Trip)), 2.89 (sep, 2H, J = 6.9 Hz, *p*-*CH*Me$_2$ (Trip)), 3.65 (sep, 4H, J = 6.9 Hz, *o*-*CH*Me$_2$ (Trip)), 7.06 (s, 4H, *m*-H (Trip)). MS (LSIMS+): *m*/*z* (%) = 799 (37) $[M]^+$, 603 (13) $[M - \text{dmit}]^+$, 399 (100) $[M - \text{dmit} - \text{Trip}]^+$.

Reaction of $[\text{SnMe}_2(\text{bdt})]$ with $[\text{NiBr}(\text{Mes})(\text{PPh}_3)_2]$

To a stirred solution of $[\text{SnMe}_2(\text{bdt})]$ (0.087 g, 0.3 mmol) in acetone (20 ml) was added $[\text{NiBr}(\text{Mes})(\text{PPh}_3)_2]$ (0.235 g, 0.3 mmol). After 5 h of stirring at room temperature or 2 h of reflux there was a red precipitate which was identified as $[\text{Ni}(\text{bdt})(\text{PPh}_3)]_2$ (**6**). Then the solvent was evaporated under reduced pressure and a new yellow solid precipitated and was identified as $[\text{Ni}(\text{Mes})(\text{bdtMes})(\text{PPh}_3)]$ (**8**). The residue was chromatographed on silica gel using dichloromethane–hexane (1 : 1) as the eluent to give in order of elution: $[\text{Ni}(\text{bdt})(\text{PPh}_3)_2]$ (**10**) and $\{\text{bdt}(\text{Mes})_2\}$ (**11**).

$[\text{Ni}(\text{bdt})(\text{PPh}_3)]_2$, (**6**). Yield: 45% (5 h); 50% (reflux) (based on nickel). Anal. calcd for $C_{48}H_{38}Ni_2P_2S_4$: C, 62.50; H, 4.15; S, 13.90. Found: C, 62.38; H, 4.39; S, 13.72. Mp (°C): 220. IR: ν(C=C) 1420 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.68 (d, 2H, *J* = 8.1 Hz, H$_1$), 6.05 (dt, 2H, *J* = 8.1, 1.2 Hz, H$_2$), 6.50 (dt, 2H, *J* = 8.1, 1.2 Hz, H$_3$), 6.67 (dd, 2H, *J* = 8.1, 1.2 Hz, H$_4$), 7.21–7.58 (m, 24H, PPh$_3$), 7.71–7.78 (m, 6H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 33.0 (s). MS (LSIMS+): *m*/*z* (%) = 922 (15) $[M]^+$, 660 (25) $[M - \text{PPh}_3]^+$. Cryoscopic molecular weight: 891.

$[\text{Ni}(\text{Mes})(\text{bdtMes})(\text{PPh}_3)]_2$ (**8**), yellow solid. Yield: 20% (5 h); 18% (reflux) (based on nickel). Anal. calcd for $C_{42}H_{41}NiPS_2$: C, 72.11; H, 5.91; S, 9.17. Found: C, 72.39; H, 5.74; S, 9.34. Mp (°C): 175. IR: ν(Mes): 1588, 856 cm^{-1}; ν(C=C): 1420 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.94 (s, 6H, *o*-Me (Mes)), 1.99 (s, 3H, *p*-Me (Mes)), 2.06 (s, 6H, *o*-Me (Mes)), 2.15 (s, 3H, *p*-Me (Mes)), 6.02 (s, 2H, *m*-H (Mes)), 6.65 (s, 2H, *m*-H (Mes)), 6.72 (dt, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 6.75 (dt, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 6.95 (dt, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 7.05 (dc, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 6.96–7.50 (m, 15H, PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 30.3 (s) (isomer a), 23.1 (isomer b). MS (LSIMS+): *m*/*z* (%) = 698 (100) $[M]^+$, 597 (44) $[M - \text{Mes}]^+$, 436 (69) $[M - \text{PPh}_3]^+$.

$[\text{Ni}(\text{bdt})(\text{PPh}_3)_2]$ (**10**), green solid. Yield: 20% (5 h); 17% (reflux) (based on nickel). Anal. calcd for $C_{42}H_{34}NiP_2S_2$: C, 69.73; H, 4.74; S, 8.86. Found: C, 69.60; H, 4.62; S, 8.64. Mp (°C): 140. IR: ν(C=C): 1441 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.26–7.47 (m, 20H, PPh$_3$, 2H (bdt)), 7.56–7.63 (m, 14H, PPh$_3$, 2H (bdt)). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 31.0 (s).

$\{\text{bdt}(\text{Mes})_2\}$ (**11**), yellow solid. Yield: 3% (5 h); 3% (reflux) (based on bdt) Anal. calcd for $C_{24}H_{26}S_2$: C, 76.14; H, 6.92; S, 16.94. Found: C, 76.30; H, 6.75; S, 16.72. Mp (°C): 165. IR: ν(Mes): 1603, 851 cm^{-1}; ν(C=C): 1435 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.27 (s, 6H, *p*-Me (Mes)), 2.35 (s, 12H, *o*-Me (Mes)), 6.36–6.39 (m, 2H, H (bdt)), 6.73–6.76 (m, 2H, H (bdt)), 6.97 (s, 4H, m-H (Mes)). LSIMS+: *m*/*z* (%) = 378 (100) $[M]^+$, 259 (37) $[M - \text{Mes}]^+$.

Reaction of $[\text{SnMe}_2(\text{bdt})]$ with $[\text{NiBr}(\text{Mes})(\text{PPh}_2\text{Me})_2]$

To a stirred solution of $[\text{SnMe}_2(\text{bdt})]$ (0.087 g, 0.3 mmol) in acetone (20 ml) was added $[\text{NiBr}(\text{Mes})(\text{PPh}_2\text{Me})_2]$ (0.197 g, 0.3 mmol). After 5 h of stirring at room temperature or 2 h of reflux, the solvent was evaporated under reduced pressure and the residue chromatographed on silica gel using dichloromethane–hexane (1 : 1) as the eluent to give, in order of elution: $\{\text{bdt}(\text{Mes})_2\}$ (**11**) [yield: 17% (5 h); 16% (reflux) (based on bdt)], $[\text{Ni}(\text{Mes})(\text{bdtMes})(\text{PPh}_2\text{Me})]$ (**9**), $[\text{Ni}(\text{bdt})(\text{PPh}_2\text{Me})]_2$ (**7**), $[\text{Ni}_3(\text{bdt})_3(\text{PPh}_2\text{Me})_2]$ (**12**) and $[\text{Ni}(\text{bdtMes})_2]$ (**13**).

$[\text{Ni}(\text{Mes})(\text{bdtMes})(\text{PPh}_2\text{Me})]$ (**9**). Yield: 16% (5 h); 10% (reflux) (based on nickel) Anal. calcd for $C_{37}H_{39}NiPS_2$: C, 69.71; H, 6.16; S, 10.06. Found: C, 69.85; H, 6.04; S, 10.38. Mp (°C): 180. IR: ν(Mes): 1602, 851 cm^{-1}; ν(C=C): 1442 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.10 (d, 3H, *J* = 9.5 Hz, PPh$_2$*Me*), 1.85 (s, 6H, *o*-Me (Mes)), 2.03 (s, 3H, *p*-Me (Mes)), 2.11 (s, 6H, *o*-Me (Mes)), 2.13 (s, 3H, *p*-Me (Mes)), 6.23 (s, 2H, *m*-Mes)), 6.61 (s, 2H, *m*-Mes)), 6.67 (dd, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 6.72 (dt, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 6.92 (dt, 1H, J = 7.9, 1.9 Hz, H (bdt)), 7.12 (dc, 1H, *J* = 7.9, 1.9 Hz, H (bdt)), 7.40–7.41 (m, 8H, P*Ph*$_2$Me), 7.76–7.77 (m, 2H, P*Ph*$_2$Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 15.9 (s) (isomer a), 10.01 (s) (isomer b). MS (LSIMS+): *m*/*z* (%) = 636 (32) $[M]^+$, 517 (22) $[M - \text{Mes}]^+$, 436 (55) $[M - \text{PPh}_2\text{Me}]^+$.

$[\text{Ni}(\text{bdt})(\text{PPh}_2\text{Me})]_2$ (**7**), red solid. Yield: 40% (5 h); 45% (reflux) (based on nickel) Anal. calcd for $C_{38}H_{34}Ni_2P_2S_4$: C, 57.17; H, 4.29; S, 16.04. Found: C, 57.32; H, 4.12; S, 15.98. Mp (°C): 158. IR: ν(C=C): 1443 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.42 (d, 6H, *J* = 9.2 Hz, PPh$_2$*Me*), 5.75 (d, 2H, *J* = 7.8 Hz, H (bdt)), 6.29 (dt, 2H, *J* = 7.8, 1.0 Hz, H (bdt)), 6.75 (dt, 2H, *J* = 7.8, 1.0 Hz, H (bdt)), 7.00 (dd, 2H, *J* = 7.8, 1.0 Hz, H (bdt)), 7.20–7.50 (m, 16H, P*Ph*$_2$Me), 7.80–8.00 (m, 4H, P*Ph*$_2$Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 15.3 (s). MS (LSIMS+): *m*/*z* (%) = 796 (35) $[M]^+$, 598 (100) $[M - \text{PPh}_2\text{Me}]^+$, 398 (88) $[M - 2\text{PPh}_2\text{Me}]^+$. Cryoscopic molecular weight: 854.

$[\text{Ni}_3(\text{bdt})_3(\text{PPh}_2\text{Me})_2]$ (**12**), green solid. Yield: 10% (5 h); 7% (reflux) (based on nickel) Anal. calcd for $C_{44}H_{38}Ni_3P_2S_6$: C, 52.99; H, 3.84; S, 19.29. Found: C, 53.5; H, 4.15; S, 19.6. Mp (°C): 118. IR: ν(C=C): 1436 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.05 (d, 6H, *J* = 13.2 Hz, PPh$_2$*Me*), 6.49 (dd, 2H, *J* = 5.6, 3.2 Hz, H (bdt)), 7.40–7.50 (m, 14H, P*Ph*$_2$Me, 2H (bdt)), 6.94 (m, 2H, H (bdt)), 7.13–7.21 (m, 8H, 2bdt), 7.72–7.77 (m, 6H, P*Ph*$_2$Me), 7.48–7.57 (m, 10H, P*Ph*$_2$Me), 7.30–7.38 (m, 4H, P*Ph*$_2$Me). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 30.15 (s). MS (LSIMS+): *m*/*z* (%) = 597 (20) $[M - 2\text{PPh}_2\text{Me}]^+$, 797 (15) $[M - \text{PPh}_2\text{Me}]^+$, 997 (15) $[M]^+$.

$[\text{Ni}(\text{bdtMes})_2]$ (**13**), red crystals. Minority product. ^{1}H NMR (CDCl$_3$): δ 2.26 (s, 6H, *p*-Me (Mes)), 2.29 (s, 12H, *o*-Me (Mes)), 6.42–6.43 (m, 4H, H (bdt)), 6.86–6.87 (m, 4H, H (bdt)), 7.08 (s, 4H, *m*-H (Mes)). MS (LSIMS+): *m*/*z* (%) = 457 (62) $[M - \text{Mes}]^+$.

Reaction of $[\text{SnMe}_2(\text{tdt})]$ with $[\text{NiBr}(\text{Mes})(\text{PPh}_3)_2]$

To a stirred solution of $[\text{SnMe}_2(\text{tdt})]$ (0.091 g, 0.3 mmol) in acetone (20 ml) was added $[\text{NiBr}(\text{Mes})(\text{PPh}_3)_2]$ (0.235 g, 0.3 mmol). After 5 h of stirring at room temperature or 2 h of reflux the solvent was evaporated under reduced pressure and the residue chromatographed on silica gel using dichloromethane–hexane (1 : 1) as the eluent to give, in order of elution: $\{\text{tdt}(\text{Mes})_2\}$ (**14**), $[\text{Ni}(\text{Mes})(\text{tdtMes})(\text{PPh}_3)]$ (**15**), $[\text{Ni}(\text{tdt})(\text{PPh}_3)]_2$ (**17**) and $[\text{Ni}(\text{tdtMes})_2]$ (**19**).

$\{\text{tdt}(\text{Mes})_2\}$ (**14**), yellow solid. Yield: 18% (5 h); 18% (reflux) (based on tdt). Anal. calcd for $C_{25}H_{28}S_2$: C, 76.48; H, 7.19; S, 16.33. Found: C, 76.30; H, 7.41; S, 16.10. Mp (°C): 80. IR: ν(Mes): 1583, 849 cm^{-1}; ν(C=C): 1434 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.06 (s, 3H, Me (tdt)), 2.31 (s, 3H, *p*-Me (Mes)), 2.32 (s, 3H, *p*-Me (Mes)), 2.42 (s, 12H, *o*-Me (Mes)), 6.21–6.23 (m, 1H, H (tdt)), 6.36 (dd, 1H, *J* = 8.0, 1.8 Hz, H (tdt), 6.59–6.60 (m, 1H, H (tdt)), 6.99 (s, 2H, *m*-H (Mes)), 7.00 (s, 2H, *m*-H (Mes)). MS (LSIMS+): *m*/*z* (%) = 392 (100) $[M]^+$.

[Ni(Mes)(tdtMes)(PPh_3)] (**15**), yellow solid. Yield: 20% (5 h); 17% (reflux) (based on nickel) Anal. calcd for $C_{43}H_{43}NiPS_2$: C, 72.38; H, 6.07; S, 8.99. Found: C, 72.52; H, 6.20; S, 8.70. Mp (°C): 173. IR: *ν*(Mes): 1573, 855 cm^{-1}, *ν*(C=C): 1433 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 1.95 (s, 6H, *o*-Me (Mes)), 1.99 (s, 3H, *p*-Me (Mes)), 2.04 (s, 6H, *o*-Me (Mes)), 2.16 (s, 3H, Me (tdt)), 2.17 (s, 3H, *p*-Me (Mes)), 6.01 (s, 2H, *m*-H (Mes)), 6.64 (s, 2H, *m*-H (Mes)), 6.52–6.57 (m, 1H, H (tdt)), 6.50–6.57 (m, 1H, H (tdt)), 7.00–7.06 (m, 1H, H (tdt)), 7.16–7.47 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ* 29.9 (s) (isomer a), 30.0 (s) (isomer b), 22.9 (s) (isomer c), 22.8 (s) (isomer d). MS (LSIMS+): *m*/*z* (%) = 712 (75) $[M]^+$, 593 (54) $[M - Mes]^+$, 450 (100) $[M - PPh_3]^+$.

$[Ni(tdt)(PPh_3)]_2$ (**17**), red solid. Yield: 51% (5 h); 58% (reflux) (based on nickel) Anal. calcd for $C_{50}H_{42}Ni_2P_2S_4$: C, 63.18; H, 4.45; S, 13.49. Found: C, 63.36; H, 4.21; S, 13.66. Mp (°C): 150. IR: *ν*(C=C): 1442 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* (isomer a) 1.62 (s, 3H, Me(1) (tdt)), 1.88 (s, 3H, Me(2) (tdt)), 5.48 (d, 1H, $J = 4.1$ Hz, H_1), 5.65 (dd, 1H, $J = 8.1, 4.1$ Hz, H_4), 5.87 (d, 1H, $J = 8.1$ Hz, H_5), 6.33 (d, 1H, $J = 8.1$ Hz, H_2), 6.46 (s, 1H, H_6), 6.56 (d, 1H, $J = 8.1$ Hz, H_3), 7.10–7.30 (m, 18H, PPh_3), 7.60–7.80 (m, 12H, PPh_3); *δ* (isomer b) 1.62 (s, 6H, Me (tdt)), 5.48 (s, 2H, H_1), 6.33 (d, 2H, $J = 8.1$ Hz, H_2), 6.56 (d, 2H, $J = 8.1$ Hz, H_3), 7.10–7.30 (m, 18H, PPh_3), 7.60–7.80 (m, 12H, PPh_3); *δ* (isomer c) 1.88 (s, 6H, Me (tdt)), 5.65 (dd, 2H, $J = 8.1, 4.1$ Hz, H_4), 5.87 (d, 2H, $J = 8.1$ Hz, H_5), 6.46 (s, 2H, H_6), 7.10–7.30 (m, 18H, PPh_3), 7.60–7.80 (m, 12H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta_A = 33.5$, $\delta_B = 32.8$, $J_{AB} = 6.8$ Hz (isomer a); *δ* 33.3 (s) (isomer b); *δ* 32.9 (s) (isomer c). MS (LSIMS+): *m*/*z* (%) = 950 (10) $[M]^+$, 688 (40) $[M - PPh_3]^+$. Cryoscopic molecular weight: 868.

$[Ni(tdtMes)_2]$ (**19**). Minority product. ^1H NMR ($CDCl_3$): *δ* 1.55 (s, 6H, Me (tdt)), 1.70 (s, 6H), 2.36 (d, 12H, $J = 11.4$ Hz), 5.79–5.80 (m, 4H), 6.80–7.00 (m, 6H). MS (LSIMS+): *m*/*z* (%) = 604 (28) $[M]^+$, 485 (42) $[M - Mes]^+$, 333 (44) $[M - Mes - tdt]^+$.

Reaction of $[SnMe_2(tdt)]$ with $[NiBr(Mes)(PPh_2Me)_2]$

To a stirred solution of $[SnMe_2(tdt)]$ (0.091 g, 0.3 mmol) in acetone (20 ml) was added $[NiBr(Mes)(PPh_2Me)_2]$ (0.197 g, 0.3 mmol). After 5 h of stirring at room temperature or 2h of reflux the solvent was evaporated under reduced pressure and the residue chromatographed on silica gel using dichloromethane–hexane (1 : 1) as the eluent to give, in order of elution: $\{tdt(Mes)_2\}$ (**14**) [yield: 20% (5 h); 20% (reflux) (based on tdt)], [Ni(Mes)(tdtMes)(PPh_2Me)] (**16**) and $[Ni(tdt)(PPh_2Me)_2]$ (**18**).

[Ni(Mes)(tdtMes)(PPh_2Me)] (**16**). Yield: 17% (5 h); 13% (reflux) (based on nickel) Anal. calcd for $C_{38}H_{41}NiPS_2$: C, 70.05; H, 6.34; S, 9.84. Found: C, 70.45; H, 6.02; S, 9.76. Mp (°C): 145. IR: *ν*(Mes): 1575, 844 cm^{-1}; *ν*(C=C): 1434 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* 1.06 (d, 3H, $J = 9.5$ Hz, PPh_2*Me*), 1.90 (s, 6H, *o*-Me (Mes)), 2.07 (s, 6H, *p*-Me (Mes)), 2.15 (s, 6H, *o*-Me (Mes)), 2.17 (s, 3H, Me (tdt)), 6.28 (s, 2H, *m*-H (Mes)), 6.65 (s, 2H, *m*-H (Mes)), 6.50–6.68 (m, 1H, H (tdt)), 6.76–6.82 (m, 1H, H (tdt)), 7.12–7.20 (m, 1H, H (tdt)), 7.30–7.80 (m, 10H, P*Ph₂*Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ* 15.8 (s) (isomer a); 15.7 (s) (isomer b); 9.9 (s) (isomer c); 9.8 (s) (isomer d). MS (LSIMS+): *m*/*z* (%) = 650 (40) $[M]^+$, 531 (27) $[M - Mes]^+$, 450 (100) $[M - PPh_2Me]^+$.

$[Ni(tdt)(PPh_2Me)]_2$ (**18**), red solid. Yield: 45% (5 h); 50% (reflux) (based on nickel). Anal. calcd. for $C_{40}H_{38}Ni_2P_2S_4$: C, 58.14; H, 4.63; S, 15.52. Found: C, 58.02; H, 4.41; S, 15.75. Mp (°C): 110. IR: *ν*(C=C): 1440 cm^{-1}. ^1H NMR ($CDCl_3$): *δ* (isomer a) 1.38 (d, 3H, $J = 8.7$ Hz, PPh_2*Me(2)*), 1.46 (d, 3H, $J = 8.7$ Hz, PPh_2*Me(1)*), 1.79 (s, 3H, Me(1) (tdt)), 2.05 (s, 3H, Me(2) (tdt)), 5.58 (s, 1H, H_1), 5.74 (dd, 1H, $J = 7.7, 1.8$ Hz, H_4), 6.10 (d, 1H, $J = 7.8$ Hz, H_5), 6.63 (d, 1H, $J = 7.9$ Hz, H_2), 6.81 (s, 1H, H_6), 6.92 (dd, 1H, $J = 5.8, 2.3$ Hz, H_3), 7.26–7.99 (m, 20H, P*Ph₂*Me); *δ* (isomer b) 1.46 (d, 6H, $J = 8.7$ Hz, PPh_2*Me*), 1.79 (s, 6H, Me (tdt)), 5.58 (s, 2H, H_1), 6.63 (d, 2H, $J = 7.9$ Hz, H_2), 6.92 (dd, 2H, $J = 5.8, 2.3$ Hz, H_3), 7.26–7.99 (m, 20H, P*Ph₂*Me); *δ* (isomer c) 1.38 (d, 6H, $J = 8.7$ Hz, PPh_2*Me*), 2.05 (s, 6H, Me (tdt)), 5.74 (dd, 2H, $J = 7.7$,

Table 1 Summary of crystallographic data for complexes **3**, **5**, **12** and **13**

	3	**5**	**12**	**13**
Empirical formula	$C_{39}H_{37}Ni\ PS_5$	$C_{36}H_{46}S_{10}$	$C_{44}H_{38}Ni_3P_2S_6$	$C_{30}H_{30}NiS_4$
Formula weight	755.67	799.33	997.17	577.49
Temperature/K	150(2)	173(2)	100(2)	173(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	10.329(3)	12.147(2)	18.788(4)	9.97(17)
b/Å	18.632 (4)	12.389(3)	11.471(3)	11.228(3)
c/Å	18.775(5)	15.000(3)	19.393(5)	11.940(3)
α/°	90	74.124(4)	90	90
β/°	93.717(3)	75.996(4)	93.476(6)	94.46(3)
γ/°	90	70.253(4)	90	90
V/Å^3	3605.6(16)	2015.3(7)	4171.7(17)	1332(23)
Z	4	2	4	2
D_c/Mg m^{-3}	1.392	1.317	1.588	1.440
μ/mm^{-1}	0.900	0.572	1.750	1.060
Crystal size/mm	0.15 × 0.15 × 0.1	0.16 × 0.12 × 0.05	0.08 × 0.05 × 0.03	0.26 × 0.2 × 0.12
θ range for data collection/°	1.54 to 25.04	1.43 to 28.3	2.06 to 27.00	4.01 to 25.03
R(int)	0.1010	0.0684	0.0856	0.0840
$R1^a$, w$R2^b$ $[I > 2\sigma(I)]$	0.0398, 0.1008	0.0750, 0.2030	0.0503, 0.0791	0.0266, 0.0687
Min., max. $\Delta\rho$/e Å^{-3}	0.387, –0.504	0.530, –0.567	0.876, –0.600	0.258, –0.3

[a] $R1 = \sum\|F_o| - \sum|F_c|/|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2]\}^{1/2}$.

1.8 Hz, H_4), 6.10 (d, 2H, $J = 7.8$ Hz, H_5), 6.81 (s, 2H, H_6), 7.26–7.99 (m, 20H, PPh_2Me). $^{31}P\{^1H\}$ NMR (–60 °C, $CDCl_3$): $\delta_A = 16.4$, $\delta_B = 16.7$, $J_{AB} = 7.2$ Hz (isomer a); δ 16.8 (s) (isomer b); δ 16.5 (s) (isomer c). MS (LSIMS+): m/z (%) = 824 (45) $[M]^+$, 626 (100) $[M - PPh_2Me]^+$. Cryoscopic molecular weight: 776.

Crystallographic studies

Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether or hexane into dichloromethane solutions. A summary of the fundamental crystal and refinement data of compounds **3**, **5**, **12** and **13** is given in Table 1. The crystals were mounted on glass fibers with inert oil and centered on a Enraf Nonius Kappa CCD area detector in the case of **3**, a Bruker-Siemens Smart CCD diffractometer for **5** and **12**, and in a Stoe-Siemens four circle diffractometer for **13**, using in all cases monochromated Mo Kα radiation ($\lambda = 0.7107$ Å), scan type θ–2θ. Cell constants were refined by setting angles for 1180 reflections in the 2θ range 20.06–46.17° for **13**. Absorption corrections were applied on the basis of ψ scans for **13** and using SORTAV[80] and SADABS[81] programs for **3** and **5** and **12** respectively. In the case of **13** the low C–C bond precision is a result of weak scattering by the crystal.

The structures were solved by direct methods using SHELXS.[82]

Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at geometrically determined positions, riding on their respective carbon atoms. Full-matrix least squares refinement was carried out using SHELX97[83] and SHELXTL[84] software package, minimizing $\omega(F_0^{2*} - F_c^2)^2$. Weighted R factors (R_w) and all goodness of fit S values are based on F^2; conventional R factors (R) are based on F.

Conclusions

In conclusion, we present here dithiolate transfer reactions between $[SnMe_2(S–S)]$ and $[NiBrR'(PR_3)_2]$ (S–S = dmit, bdt, tdt; R′ = Mes, Trip) in a 1 : 1 ratio. Instead of the reaction being solely transfer of dithiolate to give the dinuclear $[Ni_2(\mu\text{-}S–S)R'_2(PR_3)_4]$ derivatives (neither isolated nor detected), the transfer reaction occurred along with the concatenation of S–C and S–S coupling reactions, mediated by nickel and tin organometallic complexes, affording a great variety of organic $\{S–SR'\}_2$ or $\{R'S–SR'\}$ and organometallic $[NiR'(S–SR')(PR_3)_2]$ compounds. The main point of this work is that these Ni and Sn mediated organic reactions can be used for the synthesis of thio or thiolate organic- and organometallic materials not accessible by other methods.

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