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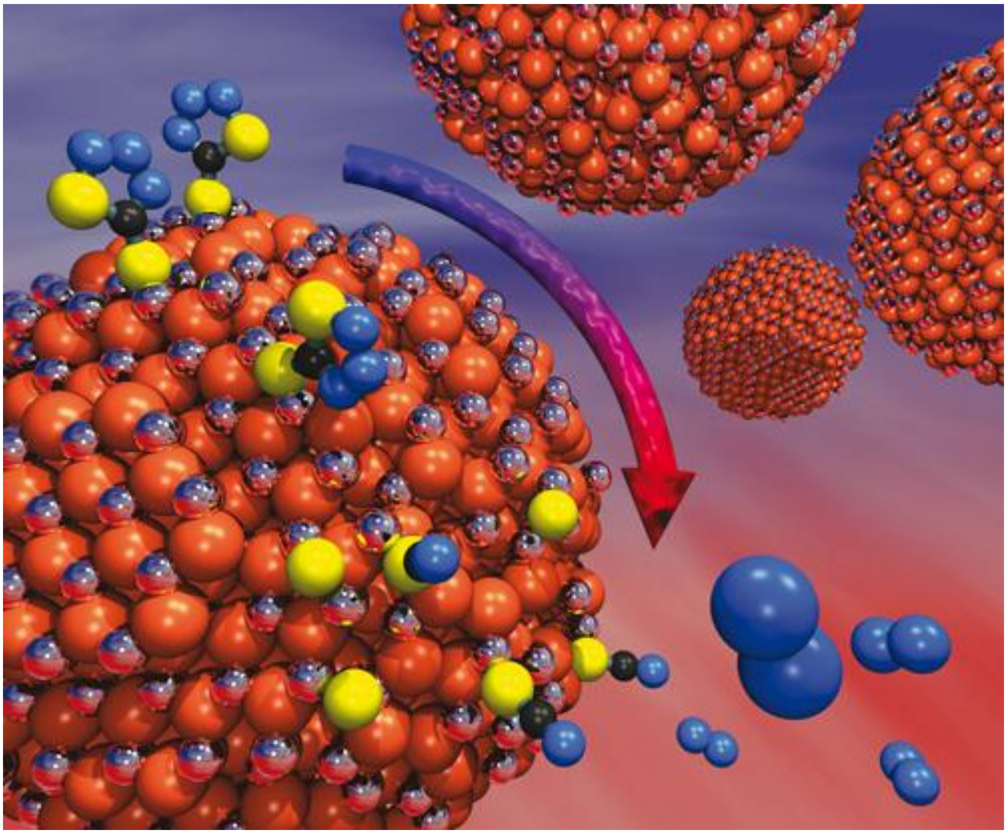

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PAPER

Substituent effects on Ni–S bond dissociation energies and kinetic stability of nickel arylthiolate complexes supported by a bis(phosphinite)-based pincer ligand†

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Pincer complexes of the type [2,6-($R_2PO)_2C_6H_3$]NiSC_6H_4Z (R = Ph and i-Pr; Z = *p*-OCH_3, *p*-CH_3, H, *p*-Cl, and *p*-CF_3) have been synthesized from [2,6-($R_2PO)_2C_6H_3$]NiCl and sodium arylthiolate. X-ray structure determinations of these thiolate complexes have shown a somewhat constant Ni–S bond length (approx. 2.20 Å) but an almost unpredictable orientation of the thiolate ligand. Equilibrium constants for various thiolate exchange (between a nickel thiolate complex and a free thiol, or between two different nickel thiolate complexes) reactions have been measured. Evidently, the thiolate ligand with an electron-withdrawing substituent prefers to bond with "[2,6-($Ph_2PO)_2C_6H_3$]Ni" rather than "[2,6-(i-$Pr_2PO)_2C_6H_3$]-Ni", and bonds least favourably with hydrogen. The reactions of the thiolate complexes with halogenated compounds such as $PhCH_2Br$, CH_3I, CCl_4, and Ph_3CCl have been examined and several mechanistic pathways have been explored.

Introduction

Late transition metal complexes bearing anionic heteroatomic ligands such as RO^-, R_2N^-, and RS^- are fundamentally important for their crucial roles in catalytic carbon–heteroatom bond forming reactions.[1] The reactivity of the MX moiety (X = OR, NR_2, and SR) toward carbon-based electrophiles is often higher than that of the corresponding HX species. Molecular orbital analysis has suggested that π-symmetry interaction between an occupied metal d orbital and a filled heteroatom p orbital results in a higher energy π-orbital and thereby enhances the nucleophilicity of the metal-bound heteroatomic ligands.[2] An alternative explanation has echoed Drago's electrostatic–covalent (E–C) model[3] and emphasized the electrostatic (or ionic) component of bonding in M–X bonds.[4] For complexes involving late transition metals, especially those in the first row, M–X bonds are significantly polarized as compared to H–X bonds. Accordingly, anionic heteroatomic ligands attached to late transition metals are more nucleophilic than the neutral, metal-free HX.

During our study of cross-coupling of aryl iodides and aryl thiols catalysed by nickel bis(phosphinite) pincer complexes,[5] we became interested in the chemistry of square-planar diamagnetic nickel arylthiolate complexes that are shown in Chart 1. In a related report, Morales-Morales and co-workers have postulated that complex **1c** can react with PhI readily to form PhSPh (eqn (1)).[6] The same type of reactions could be involved in our catalytic system. However, our mechanistic studies have suggested that it is too slow to be a viable step under the catalytic conditions.[5] Nevertheless, the mixture of **1c** and PhI in DMF-d_8 at 80 °C does produce PhSPh in 5% GC yield after 24 h. We are thus curious to know how the Ni–S bond of **1c** is cleaved during this process. Given the fact that nickel radicals supported by a pincer-type ligand are known in the literature,[7] homolytic Ni–S bond dissociation is an attractive possibility. It is also likely that nucleophilic aromatic substitution of PhI takes place with the nickel-bound thiolate. A similar reaction pathway has been suggested in copper-catalysed formation of carbon–heteroatom bonds.[8,9] Prompted by these mechanistic hypotheses, we decided to study Ni–S bond dissociation energies (BDEs) and nucleophilicity of the nickel arylthiolate complexes depicted in Chart 1, with an objective to delineate how the substituents on the thiolate ligand and the phosphorus donor atoms would impact the thermodynamic and kinetic stability of

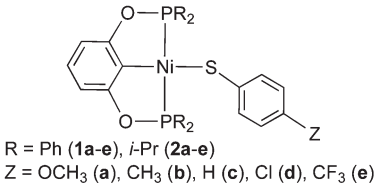

Chart 1

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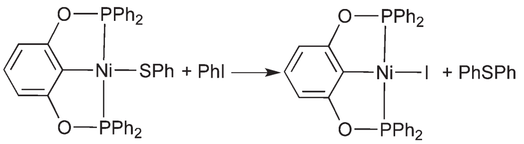
† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF and PDF formats, kinetic data, and plots of these data. CCDC 872168–872175 (complexes **1b**, **1d**, **1e**, and **2a–e**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30407d

the Ni–S bonds. Such information should not only help us to modulate the reactivity of metal thiolate complexes, but also have important mechanistic implications in various C–S bond formation reactions catalysed by transition metal complexes.[10]



1c

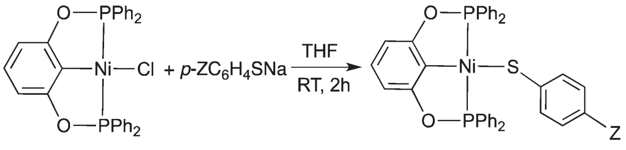
(1)

Thermodynamic data of M–S bonds of transition metal thiolate complexes are surprisingly limited in the literature, particularly for compounds containing late transition metals.[11] The nucleophilicity of metal thiolate complexes, on the other hand, are better understood due to the efforts of bioinorganic chemists to model cysteine-ligated metalloenzymes.[12] However, studies on nickel systems have been primarily focused on the electrophilic alkylation of paramagnetic thiolate complexes.[13] Of the known diamagnetic Ni(II) complexes with a terminal thiolate ligand,[14] neither BDEs nor nucleophilicity of Ni–S bonds have been examined. In this work, we will report the synthesis and structures of pincer-ligated nickel arylthiolate complexes that are shown in Chart 1. Using well-established equilibrium constant measurement[4a,15] in combination with reported S–H BDEs of substituted and unsubstituted thiophenols,[16] we will describe the electronic effects of the ligand substituents on *relative* Ni–S BDEs of the nickel thiolate complexes and analyse the nature of the Ni–S bonds with the E–C model. We will also compare the nucleophilicity of these complexes by studying the kinetics of their reaction with benzyl bromide.

Results and discussion

Synthesis and structures of nickel thiolate complexes

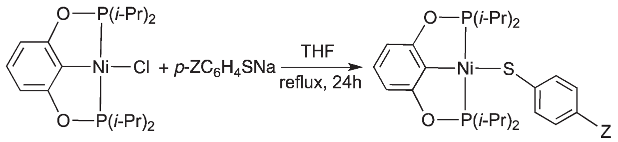
Following our previously reported procedures for the synthesis of **1a–c**,[5] room temperature reaction of [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiCl with *p*-ZC$_6$H$_4$SNa (Z = Cl and CF$_3$) in THF afforded the analogous complexes **1d** and **1e** in good yield (eqn (2)). A different series of nickel arylthiolate complexes containing isopropyl groups on the phosphorus donor atoms were prepared using a similar approach, but under refluxing conditions (eqn (3)). In contrast to many other reported nickel thiolate complexes that are prone to *S*-oxygenation by O$_2$,[17] all the thiolate complexes reported here are remarkably air stable both in solution and in the solid state.



^{Ph}LNiCl

1d (Z = Cl, *70%*)
1e (Z = CF$_3$, *81%*)

(2)



^{iPr}LNiCl

2a (Z = OCH$_3$, *78%*)
2b (Z = CH$_3$, *78%*)
2c (Z = H, *82%*)
2d (Z = Cl, *76%*)
2e (Z = CF$_3$, *72%*)

(3)

The strength of an M–S bond may be inferred from its bond length, which is sensitive to the coordination number for the metal, molecular geometry, as well as the steric and electronic properties of the ancillary ligands. When these structural features are kept the same, the bond length can be influenced by the basicity of the thiolate ligand. For example, over a range of pseudo-tetrahedral zinc thiolate complexes with an identical scorpionate-type ligand, the shortest Zn–S bond has been found in the compound bearing the most basic thiolate ligand.[18] Similar results have been described by Jensen and co-workers in their study of nickel arylthiolate complexes containing a tris(pyrazolyl)borate (Tp) ligand, although the comparison was made between complexes with different Tp ligands.[13c]

The nickel thiolate complexes reported in this paper crystallize readily, providing an excellent opportunity for a more systematic comparison of the Ni–S bond lengths. The structures of **1a** and **1c** have been reported in our previous study.[5] As representative examples, the structures of **1b** and **2b** are shown in Fig. 1 and 2, respectively. Structures and crystallographic data of other thiolate complexes are provided in ESI.† For ease of comparison, all the Ni–S bond lengths including those of **1a** and **1c** are compiled in Table 1. When the basicity of the thiolate ligand[19] decreases in going from **1a** to **1e**, Ni–S bond length is almost invariable (approx. 2.20 Å), except in **1c** where the bond [2.2338(6) Å] is slightly longer. To compensate for the longer Ni–S bond, the S1–C31 bond in **1c** [1.763(2) Å] is about 0.02 Å shorter than those of other nickel thiolate complexes. Another anomaly of **1c**

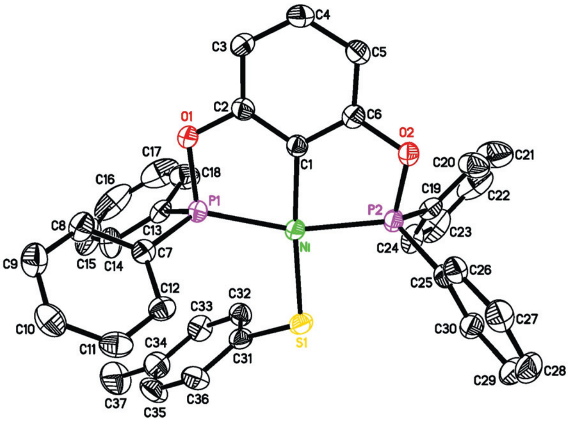


Fig. 1 ORTEP drawing of [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiSC$_6$H$_4$CH$_3$ (**1b**) at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ni–S1 = 2.1947(7), Ni–C1 = 1.907(2), Ni–P1 = 2.1555(7), Ni–P2 = 2.1452(7), S1–C31 = 1.784(3); P1–Ni–P2 = 163.10(3), P1–Ni–S1 = 103.11(3), P2–Ni–S1 = 93.79(3), C1–Ni–S1 = 174.45(7), C31–S1–Ni = 110.85(8).

is the orientation of the thiolate ligand relative to the coordination plane, which results in a dihedral angle of 72.76(5)° between planes P1–Ni–P2 and Ni–S1–C31. In contrast to this "perpendicular" geometry (Fig. 3), the thiolate ligand in other nickel complexes of the same series adopts an "in-plane" geometry with a significantly smaller dihedral angle (24.43–31.30°, see Table 2). Interestingly, in the isopropyl series **2c** has the shortest Ni–S bond [2.1734(6) Å], but other Ni–S bond lengths fall in the narrow range of 2.1908(7)–2.2191(6) Å (Table 1). The orientation of the thiolate ligand in the isopropyl series is not easily predicted either (Table 2); relatively smaller dihedral angles are found in complexes **2b** and **2c** (Fig. 4). The *ipso*-carbon–nickel bond length may also be impacted by the thiolate ligand; perhaps the ligand inducing a shorter Ni–S bond exerts greater *trans* influence on the Ni–C distance. However, as suggested by Table 3, the Ni–C bond length is rather constant, regardless of the substituents on the phosphorus atoms or the thiolate aromatic ring. Taken together, these results suggest that *the electronic effects of the supporting ligand on the bond lengths are very small and can be smaller than the uncertainty of crystal structure determination*. Additionally, crystal packing effects, offset face-to-face π-stacking interactions,[20] and C–H/π interactions[21] may play bigger roles in maintaining a relatively constant Ni–S bond length and affecting the orientation of the thiolate ligand. More importantly, the reactivity of these nickel arylthiolate complexes in solution (*vide infra*) has no correlation with the Ni–S bond lengths revealed by the X-ray studies, and the rotation of the Ni–S bonds in solution is not restricted as all the thiolate complexes display a singlet in their $^{31}P\{^1H\}$ NMR spectra.

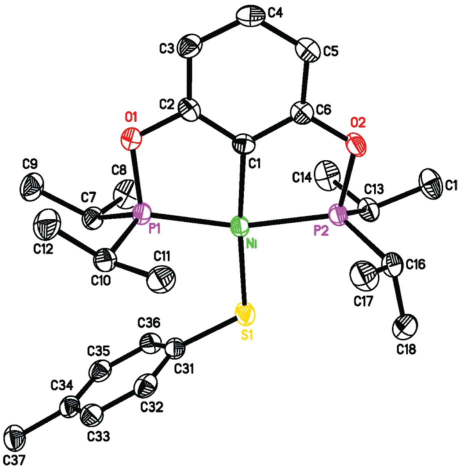


Fig. 2 ORTEP drawing of $\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiSC_6H_4CH_3$ (**2b**) at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Ni–S1 = 2.1908(7), Ni–C1 = 1.907(2), Ni–P1 = 2.1566(7), Ni–P2 = 2.1538(7), S1–C31 = 1.789(3); P1–Ni–P2 = 163.27(3), P1–Ni–S1 = 104.37(3), P2–Ni–S1 = 92.24(3), C1–Ni–S1 = 173.99(8), C31–S1–Ni = 114.07(8).

Relative bond dissociation energies (BDEs)

The absolute BDE value for an M–S bond may be determined from solution calorimetry by combining the metal thiolate complex with HCl.[11a–c] However, to address specifically the effects of ligand substituents on M–S BDEs of a series of related complexes, only the relative BDE values are needed. Such information can be conveniently obtained through equilibrium

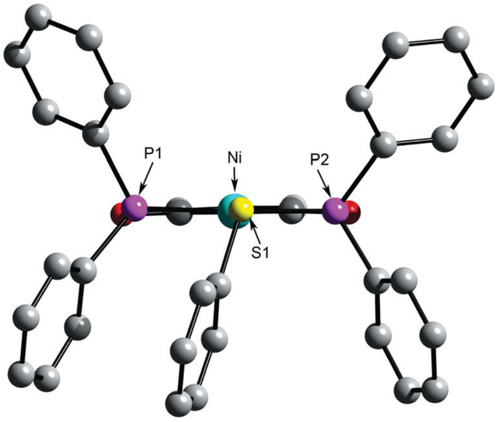


Fig. 3 Side view of **1c** illustrating the "perpendicular" orientation of the thiolate ligand.

Table 1 Ni–S bond lengths (Å) of nickel arylthiolate complexes

	Z = OCH_3 (**a**)	Z = CH_3 (**b**)	Z = H (**c**)	Z = Cl (**d**)	Z = CF_3 (**e**)
Ph series (**1a–e**)	2.1965(6)[a,b] 2.1979(10)[a,b]	2.1947(7)	2.2338(6)[a]	2.1961(5)	2.2030(10)
i-Pr series (**2a–e**)	2.2191(6)	2.1908(7)	2.1734(6)	2.2083(6)	2.2075(8)

[a] From ref. 5. [b] Complex **1a** crystallizes in two different crystal forms.

Table 2 Dihedral angles (°) between P1–Ni–P2 and Ni–S1–C31 planes in nickel arylthiolate complexes

	Z = OCH_3 (**a**)	Z = CH_3 (**b**)	Z = H (**c**)	Z = Cl (**d**)	Z = CF_3 (**e**)
Ph series (**1a–e**)	26.00(12)[a,b] 31.30(20)[a,b]	26.97(13)	72.76(5)[a]	24.43(11)	27.48(19)
i-Pr series (**2a–e**)	54.82(9)	8.49(23)	19.64(10)	42.95(7)	42.25(10)

[a] From ref. 5. [b] Complex **1a** crystallizes in two different crystal forms.

Table 3 Ni–C bond lengths (Å) of nickel arylthiolate complexes

	Z = OCH_3 (**a**)	Z = CH_3 (**b**)	Z = H (**c**)	Z = Cl (**d**)	Z = CF_3 (**e**)
Ph series (**1a–e**)	1.909(2)[a,b] 1.907(3)[a,b]	1.907(2)	1.898(2)[a]	1.909(2)	1.910(3)
i-Pr series (**2a–e**)	1.899(2)	1.907(2)	1.899(2)	1.900(2)	1.899(3)

[a] From ref. 5. [b] Complex **1a** crystallizes in two different crystal forms.

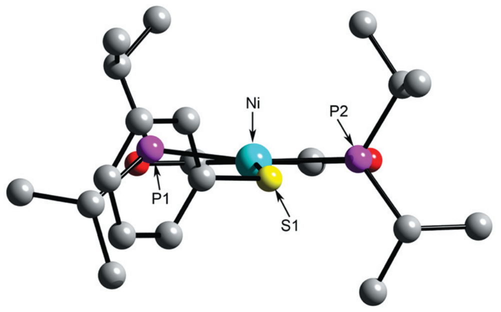


Fig. 4 Side view of **2c** illustrating the "in plane" orientation of the thiolate ligand.

Table 4 Equilibrium constants for the exchange reactions between **1c** and *para*-substituted thiophenols at 23 °C

Z	K_{eq} (in toluene-d_8)[a]	K_{eq} (in THF-d_8)[a]
OCH_3	0.92 ± 0.03	0.91 ± 0.02
CH_3	0.91 ± 0.05	0.87 ± 0.03
Cl	5.6 ± 0.6	5.7 ± 0.9
CF_3	18.9 ± 0.4	13.8 ± 0.4

[a] Average of three individual experiments.

Table 5 Relative S–H BDEs of thiols and relative Ni–S BDEs of nickel thiolate complexes **1a–e**

Z	$\Delta DH°$(S–H) (kJ mol^{-1})[a]	$\Delta DH°(^{Ph}$LNi–S) (kJ mol^{-1})
OCH_3	−8.3 ± 2.9	−8.5 ± 3.0
CH_3	−1.9 ± 2.9	−2.1 ± 3.0
Cl	3.6 ± 2.7	7.8 ± 3.0
CF_3	3.1 ± 2.8	10.3 ± 2.9

[a] Data from ref. 16*a*.

constant measurement for the exchange reactions between a metal thiolate complex (*e.g.*, **1c**) and other free thiols (eqn (4)), considering that S–H BDEs are available in the literature.[16,22]

$$\underset{\mathbf{1c}}{{}^{Ph}\text{LNiSPh}} + \text{ArSH} \xrightleftharpoons{K_{eq}} {}^{Ph}\text{LNiSAr} + \text{PhSH} \qquad (4)$$
$$\text{Ar} = p\text{-}ZC_6H_4 \ (Z = OCH_3, CH_3, Cl, CF_3)$$

At room temperature, the equilibria in eqn (4) were approached from either direction within several days. Analogous to a recent study on a related ligand exchange reaction between a PNP-pincer nickel anilide complex and PhSH,[14h] the thiolate exchange reactions shown here may proceed *via* a concerted mechanism involving thiol coordination to nickel and concurrent deprotonation by the nickel-bound thiolate. The equilibrium constants were calculated based on the integrations of ^{1}H and ^{31}P {^{1}H} NMR spectra. A potential hydrogen-bonding interaction between a thiol and a nickel thiolate could complicate the equilibrium constant measurement; however, it is not involved in our system as the SH resonances are not significantly broadened and not shifted from those of the free thiols. In addition, the equilibrium constants are temperature independent from 23 °C to 60 °C. Solvation does not appear to play a significant role either in altering the equilibria, as similar K_{eq} values have been obtained in toluene-d_8 and THF-d_8 (Table 4).

Relative Ni–S BDE, defined as the change in BDE for a nickel arylthiolate complex relative to the corresponding nickel thiophenolate complex, can be calculated from eqn (5). For reactions in which the number of particles is conserved,[23] the ΔS values are negligible, and therefore the relationship between relative Ni–S BDEs, relative S–H BDEs, and equilibrium constants is established by eqn (6). The computed gas-phase relative BDEs for different thiols[16a,22] could be used, as the equilibrium constants are insensitive to the solvent. However, the solution data (in benzene) are known,[16a] and therefore preferred in our calculations along with the K_{eq} values measured in toluene-d_8. As shown in Table 5, electron-releasing groups (OCH_3 and CH_3) weaken the Ni–S bonds whereas electron-withdrawing groups (Cl and CF_3) strengthen the Ni–S bonds. Compared to relative S–H BDEs, relative Ni–S BDEs span a wider range, a consequence of less basic thiolate ligands favoring the binding of the metal over hydrogen. From an E–C model point of view, the substituent effect on the relative Ni–S BDEs highlights the importance of the electrostatic contribution in the bonding, which is present to a lesser extent in S–H bonds.

$$\begin{aligned}\Delta DH°(^{Ph}\text{LNi–S}) &= DH°(^{Ph}\text{LNi–SAr}) - DH°(^{Ph}\text{LNi–SPh}) \\ &= DH°(\text{H–SAr}) - DH°(\text{H–SPh}) - \Delta H\end{aligned} \qquad (5)$$

Since $\Delta S \approx 0$, $\Delta H \approx \Delta G$

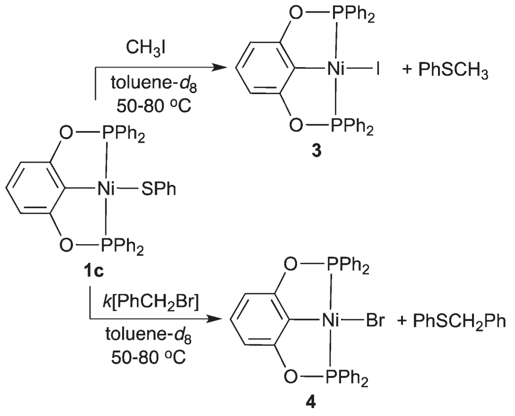
$$\Delta DH°(^{Ph}\text{LNi–S}) = \Delta DH°(\text{S–H}) + RT\ \ln K_{eq} \qquad (6)$$

Interestingly, nickel thiolate complexes undergo thiolate exchange with complexes bearing a different pincer ligand, as demonstrated in eqn (7). The reactions are markedly faster than those in eqn (4) and the equilibria are typically reached from either direction within just several hours. Mechanistic details of the exchange process, however, remain unclear to us at the moment. Fortunately, the four pincer complexes involved in each equilibrium show distinctively different ^{31}P resonances; thus

Table 6 Equilibrium constants K_{eq}' for thiolate exchange and relative Ni–S BDEs of nickel thiolate complexes **2a–e**

Z	K_{eq}' (in toluene-d$_8$)^a	$\Delta DH°(^{iPr}$LNi–S) (kJ mol^{-1})
OCH_3	1.0 ± 0.1	−8.5 ± 3.2
CH_3	0.86 ± 0.04	−2.5 ± 3.1
Cl	0.39 ± 0.03	5.5 ± 3.2
CF_3	0.26 ± 0.02	7.0 ± 3.1

^{a} Average of three individual experiments at 23 °C.



Scheme 1

Table 7 Kinetic data for the reaction of nickel thiolate complexes with $PhCH_2Br$ at 60 °C in toluene-d$_8$

Complex	Substituent Z	Rate constant k (M^{-1} s^{-1})	k_{rel}
1a	OCH_3	$2.5(2) \times 10^{-4}$	15
1b	CH_3	$1.6(2) \times 10^{-4}$	9.4
1c	H	$1.4(1) \times 10^{-4}$	8.2
1d	Cl	$4.4(2) \times 10^{-5}$	2.6
1e	CF_3	$1.7(1) \times 10^{-5}$	1
2a	OCH_3	$4.5(5) \times 10^{-4}$	26
2c	H	$1.7(1) \times 10^{-4}$	10

the equilibrium constants were conveniently measured by ^{31}P{^{1}H} NMR spectroscopy. In the cases of thiolate complexes possessing electron-releasing substituents (Table 6), the near-unity K_{eq}' values imply that relative Ni–S BDEs are constant irrespective of the pincer ligand used. On the other hand, thiolate ligands with electron-withdrawing groups clearly prefer the nickel center supported by the phenyl-substituted pincer ligand, resulting in K_{eq}' values much less than one. Relative Ni–S BDEs for complexes in the isopropyl series were calculated according to eqn (8) and are listed in Table 6. Compared to the phenyl series, these data span a more narrow range, suggesting that electrostatic interaction contributes less in the overall bonding. Salah and Zargarian have recently compared the redox potentials of nickel bis(phosphinite)-based pincer complexes with different *P*-substituents and have concluded that the pincer ligand with phenyl substituents is less electron donating than the one with isopropyl substituents.[24] One can thus view the ^{Ph}LNi moiety as a harder acid than ^{iPr}LNi, and therefore more likely to bind to a harder base such as p-$CF_3C_6H_4S^-$.

$$\underset{\mathbf{2c}}{{}^{iPr}\mathrm{LNiSPh}} + {}^{Ph}\mathrm{LNiSAr} \overset{K_{eq}'}{\rightleftharpoons} {}^{iPr}\mathrm{LNiSAr} + \underset{\mathbf{1c}}{{}^{Ph}\mathrm{LNiSPh}} \tag{7}$$

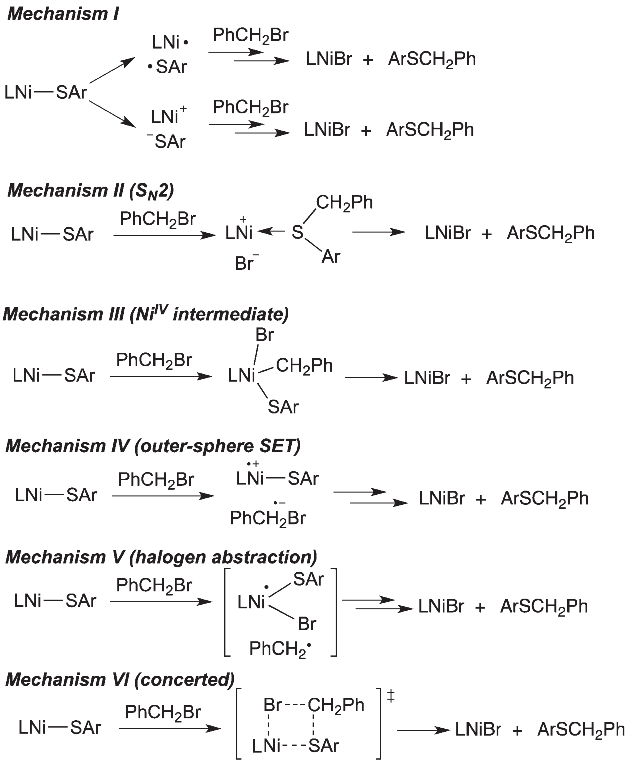
Ar = p-ZC_6H_4 (Z = OCH_3, CH_3, Cl, CF_3)

$$\Delta DH°({}^{iPr}\mathrm{LNi{-}S}) = \Delta DH°({}^{Ph}\mathrm{LNi{-}S}) + RT\ \ln K_{eq}' \tag{8}$$

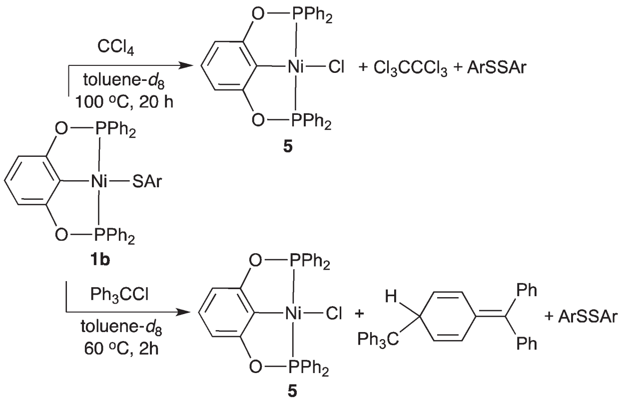
Reactivity of nickel thiolate complexes with halogenated compounds

The kinetic stability and nucleophilicity of metal thiolate complexes have often been probed by measuring the rate constants for their reactions with alkyl halides.[13,25] Iodomethane, a typical alkylating reagent for these studies, was initially chosen to react with **1c**. The reaction yields the expected nickel iodide complex **3** and $PhSCH_3$ (Scheme 1); however, the required temperature for this process (50–80 °C) is above the boiling point of CH_3I (42 °C), preventing reliable measurement of the rate constant. We then resorted to using higher boiling $PhCH_2Br$ as the alkylating reagent. In the presence of a large excess of $PhCH_2Br$ (10–20 equiv.), monitoring the disappearance of **1c** in toluene-d$_8$ by ^{1}H NMR gives the pseudo-first-order rate constant k_{obs}. Variation of [$PhCH_2Br$] establishes a linear relationship between k_{obs} and [$PhCH_2Br$], implying an overall second-order reaction (see ESI†). The second-order rate constant k for **1c** at 60 °C was determined to be $1.4(1) \times 10^{-4}$ M^{-1} s^{-1}. Rate constant measurements between 50 °C and 80 °C give $\Delta H^‡ = 61.5 \pm 0.8$ kJ mol^{-1} and $\Delta S^‡ = -135.1 \pm 2.9$ J K^{-1} mol^{-1}. The large negative entropy of activation is consistent with a bimolecular process. The kinetic behaviors of other nickel thiolate complexes toward $PhCH_2Br$ were found to be similar to that of **1c**. The second-order rate constants at 60 °C are summarized in Table 7. As seen from the phenyl series **1a–e**, the rate constant decreases when the thiolate ligand becomes less donating; under the same conditions, the reaction of **1a** is about 15 times as fast as that of **1e**. The obtained Hammett reaction constant (ρ) of −1.5 ± 0.3 implies a positive charge being built on sulfur during the reaction. Comparisons between complexes with an identical thiolate ligand show that complexes in the isopropyl series are more reactive than those in the phenyl series. For instance, the rate constant for **2a** is 1.8 times the rate constant for **1a**. This observation is consistent with the notion that the i-Pr groups are more electron donating than the Ph groups[24] and presumably help to stabilize the transition state.

Although from the net chemical transformation point of view we have described the reactions in Scheme 1 as nucleophilic reactivity of the nickel-bound thiolate, it does not necessarily define the reaction mechanism. To better understand the alkylation reactions, we have considered several mechanistic scenarios as illustrated in Scheme 2. A rate-determining homolytic or heterolytic cleavage of the Ni–S bond (mechanism I) would be inconsistent with the observed second-order reaction. Mechanism II involves an S_N2-like transition state leading to the formation of a cationic nickel complex with a thioether, which may be rapidly displaced by Br^-. Such a mechanism is supported by the negative ρ value of −1.5 determined from the kinetic studies. In addition, the reaction of **1a** with $PhCH_2Br$ in THF is approximately twice as fast as the one in toluene, presumably due to

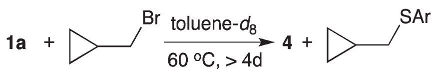


Scheme 2



Scheme 3

better stabilization of a charged species in a more polar solvent. An alternative mechanism features (concerted or S_N2-type) oxidative addition of $PhCH_2$–Br to a nickel thiolate complex (mechanism III) and invokes a formally six-coordinate Ni(IV) intermediate. Although such species are not unprecedented,[26,27] they are rarely formed *via* oxidative addition reactions.[26b,c] At a nickel center supported by a relatively electron-deficient bis(phosphinite) ligand, this is even more of a remote possibility. An outer-sphere single electron transfer (SET) mechanism[28] has been previously proposed for the reactions of alkyl halides with lithium thiolates,[29] and it may be applied to transition-metal-bound thiolates as well (mechanism IV). The large negative activation entropy (-135.1 ± 2.9 J K^{-1} mol^{-1}) obtained, however, argues against such a mechanism as the value for an outer-sphere SET process is typically small or even positive.[30] Another possible mechanism proceeds *via* the abstraction of bromine atom from $PhCH_2Br$ by the nickel thiolate complex, leading to the formation of a formally Ni(III) species (mechanism V). Analogous halogen abstraction has been proposed as the key step in nickel-catalyzed Kharasch addition reactions.[31] Furthermore, Ni(III) species bearing various pincer ligands have been spectroscopically observed or crystallographically characterized by van Koten[32] and Zargarian.[33] Such a mechanism is certainly valid in the case of reactions involving weak carbon–halogen bonds. When a solution of thiolate complex **1b** in toluene-d_8 was treated with CCl_4 at 100 °C, in addition to the expected nickel chloride complex **5**,[6] both Cl_3CCCl_3 and ArSSAr were cleanly produced (Scheme 3), as suggested by NMR and GC-MS. This result supports the formation of radical intermediates $^{\cdot}CCl_3$ and $ArS^{\cdot}$ most likely as a result of halogen abstraction. Similarly, **1b** can abstract chlorine from Ph_3CCl to generate trityl radical, which is known to dimerize to make the Gomberg dimer.[34] In an attempt to generate a radical clock,[35] we also examined the reaction between **1a** and cyclopropylmethyl bromide (eqn (9)). The alkylation reaction is significantly slower than the one with $PhCH_2Br$. More importantly, no ring-opening product was observed, which is inconsistent with the halogen abstraction and SET mechanisms. In addition to the S_N2-type mechanism described earlier, we cannot rule out a σ-bond-metathesis-like mechanism[36] in which Ni–S bond breaking and C–S bond making take place simultaneously (mechanism VI). Both mechanisms would suggest that the alkylation reaction is very sensitive to the groups around the carbon center. Indeed, we have observed that the reaction of **1a** with $PhCH_2Br$ at 60 °C is twice as fast as the one with $PhCHBrCH_3$ under the same conditions.



(9)

Conclusions

We have synthesized several new nickel thiolate complexes by varying substituents on the thiolate ligand and phosphorus donors of a bis(phosphinite)-based pincer ligand, and we have systematically compared their Ni–S bond lengths, Ni–S BDEs, as well as their kinetic stability toward halogenated compounds. In contrast to previous studies on other metal thiolate complexes,[13c,18] Ni–S bond lengths in our nickel pincer complexes are neither affected by the basicity of the thiolate ligand nor by the pincer *P*-substituents. However, Ni–S bond strengths are clearly influenced by the electronic effect of the thiolate *para*-substituent; in general, having an electron withdrawing group leads to a stronger Ni–S bond. The sensitivity of Ni–S bond strength toward changes in the thiolate substituent is dependent on the electronic property conferred by the pincer unit. A less electron-donating pincer ligand makes the Ni–S bond more sensitive to changes in the thiolate substituent, which can be rationalized by increased electrostatic contribution in the bonding. The reaction of nickel thiolate complexes with $PhCH_2Br$ is more favourable when the thiolate ligand or the pincer ligand is more electron donating. Mechanistic studies have suggested that either an

S_N2-type mechanism or a σ-bond-metathesis-like mechanism is involved in these alkylation reactions.

Experimental section

General procedures

Nickel thiolate complexes were prepared under an argon atmosphere using standard Schlenk techniques. Once formed, they can be handled in air without noticeable decomposition. Dry and oxygen-free solvents (THF, toluene, and CH_2Cl_2) were collected from an Innovative Technology solvent purification system and used throughout the experiments. Hexanes were purchased from commercial sources and used without purification or degassing. Toluene-d_8 was distilled from Na and benzophenone under an argon atmosphere. $[2,6\text{-}(Ph_2PO)_2C_6H_3]NiCl$,[6] $\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiCl$,[33b] and **1a–c**,[5] were prepared as described in the literature.

Synthesis of $[2,6\text{-}(Ph_2PO)_2C_6H_3]NiSC_6H_4Cl$ (1d). To a suspension of NaH (48 mg, 2.0 mmol) in 30 mL of THF was added 4-chlorobenzenethiol (289 mg, 2.0 mmol) at 0 °C under an argon atmosphere. The resulting mixture was warmed to room temperature and stirred for 1 h followed by the addition of $[2,6\text{-}(Ph_2PO)_2C_6H_3]NiCl$ (572 mg, 1.0 mmol). After stirring at room temperature for another 2 h, the volatiles were removed under vacuum and the residue was extracted with toluene and filtered through a pad of Celite. Removal of toluene under vacuum produced a red solid, which was recrystallized from CH_2Cl_2–hexanes (1 : 2) to give **1d** as deep red crystals (476 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.83–7.80 (m, *Ar*, 8H), 7.52–7.39 (m, *Ar*, 12H), 7.10 (t, J_{H-H} = 8.0 Hz, *Ar*, 1H), 6.94 (d, J_{H-H} = 8.3 Hz, *Ar*, 2H), 6.67 (d, J_{H-H} = 8.0 Hz, *Ar*, 2H), 6.37 (d, J_{H-H} = 8.3 Hz, *Ar*, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 166.3 (t, J_{C-P} = 11.1 Hz), 142.7 (t, J_{C-P} = 7.7 Hz), 135.0, 132.6, 132.4, 132.2 (t, J_{C-P} = 6.9 Hz), 131.6, 129.6, 128.7, 128.6 (t, J_{C-P} = 5.1 Hz), 127.0, 106.3 (t, J_{C-P} = 6.8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 148.2. Anal. Calcd for $C_{36}H_{27}ClNiO_2P_2S$: C, 63.61; H, 4.00; Cl, 5.22. Found: C, 63.35; H, 3.92; Cl, 5.47.

$[2,6\text{-}(Ph_2PO)_2C_6H_3]NiSC_6H_4CF_3$ (1e) was prepared in 81% yield by a procedure similar to that used for **1d**. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.86–7.81 (m, *Ar*, 8H), 7.50–7.37 (m, *Ar*, 12H), 7.16–7.14 (m, *Ar*, 3H), 6.71 (d, J_{H-H} = 8.0 Hz, *Ar*, 2H), 6.66 (d, J_{H-H} = 8.1 Hz, *Ar*, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 166.5 (t, J_{C-P} = 11.2 Hz), 150.4 (t, J_{C-P} = 5.6 Hz), 133.6, 132.6, 132.4, 132.1 (t, J_{C-P} = 7.1 Hz), 131.8, 130.0, 128.7 (t, J_{C-P} = 5.1 Hz), 124.8 (q, J_{C-F} = 272.0 Hz, CF_3), 124.3 (q, J_{C-F} = 32.0 Hz, CCF_3), 123.7 (q, J_{C-F} = 3.8 Hz), 106.5 (t, J_{C-P} = 6.8 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 147.0. Anal. Calcd for $C_{37}H_{27}F_3NiO_2P_2S$: C, 62.30; H, 3.82; F, 7.99. Found: C, 62.12; H, 3.70; F, 8.10.

Synthesis of $\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiSC_6H_4OCH_3$ (2a). To a suspension of NaH (120 mg, 5.0 mmol) in 30 mL of THF was added 4-methoxybenzenethiol (700 mg, 5.0 mmol) at 0 °C under an argon atmosphere. The resulting mixture was warmed to room temperature and stirred for 1 h. $\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiCl$ (436 mg, 1.0 mmol) was then added, and the reaction mixture was refluxed for 24 h. After cooling down to room temperature, the volatiles were removed under vacuum and the residue was extracted with toluene and filtered through a pad of Celite. Removal of toluene under vacuum followed by recrystallization in hexanes produced an orange solid of **2a** (421 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.35 (d, J_{H-H} = 8.6 Hz, *Ar*, 2H), 6.94 (t, J_{H-H} = 8.0 Hz, *Ar*, 1H), 6.63 (d, J_{H-H} = 8.6 Hz, *Ar*, 2H), 6.43 (d, J_{H-H} = 8.0 Hz, *Ar*, 2H), 3.75 (s, OCH_3, 3H), 2.10–2.03 (m, $CH(CH_3)_2$, 4H), 1.37–1.23 (m, $CH(CH_3)_2$, 24H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 168.0 (t, J_{C-P} = 9.1 Hz), 156.8, 136.2 (t, J_{C-P} = 9.1 Hz), 135.4, 130.9 (t, J_{C-P} = 20.2 Hz), 128.4, 113.3, 104.6 (t, J_{C-P} = 6.1 Hz), 55.4 (OCH_3), 28.4 (t, J_{C-P} = 11.1 Hz, $CH(CH_3)_2$), 17.8 (t, J_{C-P} = 3.0 Hz, $CH(CH_3)_2$), 16.8 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 189.4. Anal. Calcd for $C_{25}H_{38}NiO_3P_2S$: C, 55.68; H, 7.10. Found: C, 55.69; H, 6.96.

$\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiSC_6H_4CH_3$ (2b) was prepared in 78% yield by a procedure similar to that used for **2a**. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.33 (d, J_{H-H} = 8.0 Hz, *Ar*, 2H), 6.95 (t, J_{H-H} = 8.0 Hz, *Ar*, 1H), 6.84 (d, J_{H-H} = 8.0 Hz, *Ar*, 2H), 6.44 (d, J_{H-H} = 8.0 Hz, *Ar*, 2H), 2.24 (s, CH_3, 3H), 2.12–2.05 (m, $CH(CH_3)_2$, 4H), 1.36–1.23 (m, $CH(CH_3)_2$, 24H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 168.1 (t, J_{C-P} = 9.8 Hz), 142.0 (t, J_{C-P} = 7.9 Hz), 134.3, 132.8, 131.0 (t, J_{C-P} = 20.4 Hz), 128.5, 128.2, 104.6 (t, J_{C-P} = 6.1 Hz), 28.4 (t, J_{C-P} = 11.5 Hz, $CH(CH_3)_2$), 20.9 ($ArCH_3$), 17.8 (t, J_{C-P} = 2.5 Hz, $CH(CH_3)_2$), 16.8 ($CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 189.2. Anal. Calcd for $C_{25}H_{38}NiO_2P_2S$: C, 57.38; H, 7.32. Found: C, 57.50; H, 7.15.

Synthesis of $\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiSPh$ (2c). A mixture of $\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiCl$ (152 mg, 0.35 mmol) and NaSPh (90%, technical grade, purchased from Sigma-Aldrich, 231 mg, 1.57 mmol) in 30 mL of THF was refluxed under an argon atmosphere for 24 h. After cooling, the volatiles were removed under vacuum and the residue was treated with 40 mL of toluene and then filtered through a pad of Celite. Removal of toluene under vacuum afforded **2c** as an orange solid, which was further purified by recrystallization in hexanes (146 mg, 82% yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 7.46 (d, J_{H-H} = 7.0 Hz, *Ar*, 2H), 7.05–6.93 (m, *Ar*, 4H), 6.44 (d, J_{H-H} = 7.9 Hz, *Ar*, 2H), 2.12–2.05 (m, $CH(CH_3)_2$, 4H), 1.37–1.24 (m, $CH(CH_3)_2$, 24H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 168.1 (t, J_{C-P} = 9.8 Hz), 146.3 (t, J_{C-P} = 7.7 Hz), 134.5, 130.8 (t, J_{C-P} = 20.5 Hz), 128.6, 127.4, 123.4, 104.7 (t, J_{C-P} = 6.1 Hz), 28.4 (t, J_{C-P} = 11.7 Hz, $CH(CH_3)_2$), 17.8 (t, J_{C-P} = 2.3 Hz, $CH(CH_3)_2$), 16.8 ($CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 189.0. Anal. Calcd for $C_{24}H_{36}NiO_2P_2S$: C, 56.61; H, 7.13. Found: C, 56.81; H, 7.26.

$\{2,6\text{-}[(i\text{-}Pr)_2PO]_2C_6H_3\}NiSC_6H_4Cl$ (2d) was prepared in 76% yield by a procedure similar to that used for **2a**. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.37 (d, J_{H-H} = 8.4 Hz, *Ar*, 2H), 7.00–6.94 (m, *Ar*, 3H), 6.45 (d, J_{H-H} = 7.9 Hz, *Ar*, 2H), 2.14–2.07 (m, $CH(CH_3)_2$, 4H), 1.35–1.25 (m, $CH(CH_3)_2$, 24H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, δ): 168.1 (t, J_{C-P} = 9.6 Hz), 145.2 (t, J_{C-P} = 7.7 Hz), 135.4, 130.4 (t, J_{C-P} = 20.2 Hz), 129.0, 128.7, 127.4, 104.8 (t, J_{C-P} = 6.1 Hz), 28.5 (t, J_{C-P} = 12.1 Hz, $CH(CH_3)_2$), 17.7 (t, J_{C-P} = 2.3 Hz, $CH(CH_3)_2$), 16.8 ($CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 188.8. Anal.

Calcd for $C_{24}H_{35}ClNiO_2P_2S$: C, 53.02; H, 6.49; Cl, 6.52. Found: C, 53.29; H, 6.41; Cl, 6.51.

{2,6-[(i-Pr)$_2$PO]$_2$C$_6$H$_3$}NiSC$_6$H$_4$CF$_3$ (2e) was prepared in 72% yield by a procedure similar to that used for **2a**. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 7.53 (d, $J_{H–H}$ = 8.0 Hz, *Ar*, 2H), 7.25 (d, $J_{H–H}$ = 8.0, *Ar*, 2H), 6.98 (t, $J_{H–H}$ = 8.0 Hz, *Ar*, 1H), 6.46 (d, $J_{H–H}$ = 8.0 Hz, *Ar*, 2H), 2.17–2.10 (m, C*H*(CH$_3$)$_2$, 4H), 1.34–1.25 (m, CH(C*H*$_3$)$_2$, 24H). ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$, δ): 168.1 (t, $J_{C–P}$ = 9.6 Hz), 153.2 (t, $J_{C–P}$ = 6.9 Hz), 133.9, 130.1 (t, $J_{C–P}$ = 20.4 Hz), 129.0, 125.2 (q, $J_{C–F}$ = 32.4 Hz), 124.8 (q, $J_{C–F}$ = 272.1 Hz, *C*F$_3$), 124.0 (q, $J_{C–F}$ = 3.8 Hz), 104.8 (t, $J_{C–P}$ = 6.1 Hz), 28.5 (t, $J_{C–P}$ = 12.1 Hz, *C*H(CH$_3$)$_2$), 17.6 (t, $J_{C–P}$ = 2.3 Hz, CH(*C*H$_3$)$_2$), 16.8 (CH-(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 188.2. Anal. Calcd for $C_{25}H_{35}F_3NiO_2P_2S$: C, 52.02; H, 6.11; F, 9.87. Found: C, 52.21; H, 6.07; F, 9.98.

Equilibrium constant measurement for the exchange between a nickel thiolate complex and a free thiol. Approximately equimolar amounts of **1c** and *p*-Z-C$_6$H$_4$SH (Z = OCH$_3$, CH$_3$, Cl, and CF$_3$) were mixed in toluene-d$_8$ (~0.5 mL) at room temperature (23 °C). Typically, the thiolate exchange reaction reached its equilibrium in several days. The same equilibrium was also reached from the reverse direction by mixing approximately equimolar amounts of [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiSC$_6$H$_4$Z (Z = *p*-OCH$_3$, *p*-CH$_3$, *p*-Cl, and *p*-CF$_3$) and PhSH in toluene-d$_8$ at room temperature. Equilibrium constants were calculated based on the integrations of ^{1}H and ^{31}P{^{1}H} NMR spectra. The average value from three independent experiments is reported.

Equilibrium constant measurement for the exchange between two nickel thiolate complexes. Approximately equimolar amounts of **2c** and [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiSC$_6$H$_4$Z (Z = *p*-OCH$_3$, *p*-CH$_3$, *p*-Cl, and *p*-CF$_3$) were mixed in toluene-d$_8$ at room temperature. Typically, the thiolate exchange reaction reached its equilibrium in several hours. Equilibrium constants were calculated based on the integrations of ^{31}P{^{1}H} NMR spectra. The average value from three independent experiments is reported.

Rate constant measurement for the alkylation of nickel thiolate complexes with PhCH$_2$Br. In a typical experiment, a toluene-d$_8$ (0.50 mL) solution of nickel thiolate complex (15–20 mM) was transferred to a resealable NMR tube, followed by the addition of 1,4-dioxane (2.0 µL, as an internal standard) and 10–20 equiv. of benzyl bromide. The sealed NMR tube was placed in a constant temperature oil bath (50–80 °C). Every 20 min to 5 h, the NMR tube was quickly cooled (with cold water) to room temperature and the ^{1}H NMR spectrum was recorded. Control experiments showed that at room temperature the alkylation of nickel thiolate complexes with benzyl bromide was negligible. All the reactions were carried out until they reached 3–5 half-lives. The integration of one of the thiolate aromatic resonances was compared to that of the internal standard. Diaryl sulfides produced in these processes were verified by GC-MS. The nickel products ([2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiBr and {2,6-[(i-Pr)$_2$PO]$_2$C$_6$H$_3$}NiBr were isolated from preparative scale reactions and fully characterized.

Synthesis of [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiBr from the reaction of 1c with PhCH$_2$Br. Under an argon atmosphere, the mixture of **1c** (0.25 g, 0.39 mmol) and benzyl bromide (1.0 mL, 8.4 mmol) in 20 mL of toluene was stirred at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite, followed by evaporation of the solvent under vacuum. The resulting solid was recrystallized from CH$_2$Cl$_2$–hexanes (1 : 2) to produce [2,6-(Ph$_2$PO)$_2$C$_6$H$_3$]NiBr[24] as greenish-yellow crystals (220 mg, 92% yield). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.00–7.95 (m, *Ar*, 8H), 7.51–7.42 (m, *Ar*, 12H), 7.08 (t, $J_{H–H}$ = 8.0 Hz, *Ar*, 1H), 6.63 (d, $J_{H–H}$ = 8.0 Hz, *Ar*, 2H). ^{13}C-{^{1}H} NMR (101 MHz, CDCl$_3$, δ): 167.0 (t, $J_{C–P}$ = 11.5 Hz, *Ar*), 132.7, 132.4, 132.2 (t, $J_{C–P}$ = 7.1 Hz, *Ar*), 131.8, 129.8, 128.7 (t, $J_{C–P}$ = 5.5 Hz, *Ar*), 106.6 (t, $J_{C–P}$ = 6.8 Hz, *Ar*). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$, δ): 144.8. Anal. Calcd for $C_{30}H_{23}P_2O_2NiBr$: C, 58.49; H, 3.76. Found: C, 58.37; H, 3.78.

Synthesis of {2,6-[(i-Pr)$_2$PO]$_2$C$_6$H$_3$}NiBr from the reaction of 2c with PhCH$_2$Br. Following the same procedure as above, except recrystallization was from hexanes, {2,6-[(i-Pr)$_2$PO]$_2$-C$_6$H$_3$}NiBr was isolated in 87% yield as light brown crystals. The NMR spectra of this compound are consistent with those reported in the literature.[33a,b]

X-ray structure determinations

Single crystals of nickel thiolate complexes in the phenyl series (**1b**, **1d**, and **1e**), and those in the isopropyl series (**2a–e**) were obtained from recrystallization in CH$_2$Cl$_2$–hexanes, and hexanes, respectively. Crystal data collection and refinement parameters of **1b** and **2b** are summarized in Table 8. The data for other nickel thiolate complexes can be found in ESI. Intensity data were collected at 150 K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu Kα radiation, λ = 1.54178 Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-

Table 8 Summary of crystallographic data for representative nickel thiolate complexes

	1b	2b
Empirical formula	$C_{37}H_{30}O_2P_2SNi$	$C_{25}H_{38}O_2P_2SNi$
Formula weight	659.32	523.26
Temp, K	150(2)	150(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a, Å	14.8305(4)	10.2691(2)
b, Å	9.1267(2)	11.3934(2)
c, Å	24.2462(6)	13.1019(2)
α (°)	90	88.437(1)
β (°)	105.642(1)	67.681(1)
γ (°)	90	66.738(1)
Volume, Å^3	3160.27(13)	1289.15(4)
Z	4	2
d_{calc}, g cm^{-3}	1.386	1.348
λ, Å	1.54178	1.54178
μ, mm^{-1}	2.714	3.160
No. of data collected	26 302	11 035
No. of unique data	5650	4444
R_{int}	0.0622	0.0288
Goodness-of-fit on F^2	1.024	1.032
R_1, wR_2 ($I > 2\sigma(I)$)	0.0390, 0.0987	0.0377, 0.0957
R_1, wR_2 (all data)	0.0519, 0.1069	0.0477, 0.1019

scan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters with the exception of the disordered F-atoms in **1e**. The H-atoms were either located or calculated and subsequently treated with a riding model. No solvent of crystallization is present in the lattice for any of the structures. The F-atoms of the CF_3 group in **1e** are disordered; a two-component model is given (70 : 30 occupancy, see ESI†). The crystal structures for **1b**, **1d**, **1e**, **2a–e** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers CCDC 872168–872175.

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