# Binuclear Complexes of Ni(I) from a 4-Terphenyldithiophenol

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Binuclear Complexes of Ni(I) from a 4-Terphenyldithiophenol.

Felix Koch, Hartmut Schubert, Peter Sirsch, and Andreas Berkefeld

Binuclear complexes of Ni(I) have been prepared from a 4-terphenyldithiophenol ligand. Steric effects were found to determine the formation of coordination isomeric structures that differ in the nature of metal-to-ligand bonding. Coordination of spatially demanding phosphine ligands PR₂, R = C₂H₆, C₆H₁₄, at nickel sites result in a butterfly shaped thiolate-bridged Ni₃(µ-S)₂ motif. For smaller PMe₃, the central n-system of the 4-terphenyl backbone adopts a bis-allyl like µ-syn-η²-η²-C₄H₈ structure due to significant d-π* Ni(I)-to-ligand charge transfer. Delocalisation indices δ(Ni-Ni) derived from DFT calculations provide a metric to assess the strength of electronic coupling of the Ni sites based on solid state structural data, and indicated less strong electronic coupling for the bis-allyl like structure with δ(Ni-Ni) = 0.225 as compared to 0.548 for the Ni₃(µ-S)₂ structural motif. A qualitative reactivity study toward CNCH, as an auxiliary ligand has provided first insight into the chemical properties of the bimetallic complexes presented.

Introduction

The class of binuclear complexes of Ni(I) features a remarkable structural diversity, and ligand design plays a pivotal role in this regard. One can differentiate between structural motifs in which electronic coupling of the Ni(I) ions either occurs through bonding to (i) bridging conjugated π-systems in both syn- and antarafacial fashion, (ii) bridging amido, phosphido, thiolato, sulfido, halgenido, and hydrido ligands in the form of Ni₃(µ-X)₂ cores, (iii) bridging diphosphine, and biphenyldiyli, ligands, or in the form of unsupported Ni-Ni bonds. Antiferromagnetic coupling through ligand and direct Ni-Ni bonding result in diamagnetic behaviour in most instances, albeit triplet ground state samples have been proposed as for the Ni₃(µ-Br)₂ core bound to the neutral form of a redox active 1,8-naphthyridine diimine ligand. Based on solution reactivity and VT EPR studies on solid samples dinickel biradicals coexist in thermal equilibria with diamagnetic ground states. In the biradical state the Ni-Ni interaction is non-bonding and dissociation a favourable and facile process. The reversible formation of reactive Ni(I) species appears to represent one of two major modes of reactivity displayed by binuclear Ni(I) complexes. An early example of binuclear reactivity is the tetramerisation of ethyne to cyclooctatetraene as put forward by Wilke. Despite that the exact mechanism of this process has remained unresolved, dinickel(I) complexes have been reported to catalyse reductive C-C bond formation in a cooperative fashion, to act as precursors in bimetallic catalytic group transfer reactions to form carbodiimides and isocyanates, and to activate secondary silanes for the catalytic hydrosilation of unsaturated substrates.

The capability of thiolate ligands to bridge pair metals through bis-µ-thiolate coordination aids the formation of binuclear and higher nuclearity complexes, including well characterised examples for Ni(I) of type I in Scheme 1. In the context of a reactivity study of thiolate complexes of Ni(I), Yamada and co-workers reported the structure of a binuclear Ni(I) complex with bridging arene and thiolate groups, see II in Scheme 1.

We have set out to develop the coordination chemistry of binucleating terphenyldithiophenol ligands which combine the properties of metal-sulphur and labile metal-arene bonds. Use of a dianionic ligand framework eliminates the necessity for incorporating secondary anionic ligands that might bridge the nickel ions, which may provide structural flexibility to the bimetallic core. Herein we report on the synthesis and properties of mono- and binuclear complexes of nickel with such type of ligands.

Results and discussion

Synthesis and structure of mono- and binuclear complexes 1-5

Scheme 1. General structural motifs of binuclear Ni(I) complexes with L = neutral ligand, e.g. tert-phosphine, NHC, and R = aryl, tert-alkyl, H.
The preparation of the nickel complexes followed two different protocols. The first utilises the comproportionation of Ni(II) precursors 1 and 2 with Ni(COD)$_2$, COD is 1,5-cyclooctadiene. Alternatively, reacting 4-terphenyldithiophenol with 2 equiv. of (PPh)$_3$Ni(NiMe)$_2$ as a source of Ni(I) affords bimetallic 5 directly, eliminating bis(trimethylsilyl)amine and PPh$_3$.

Ni(II) precursor complexes 1 or 2 have been prepared by salt metathesis, reacting the dipotassium salt of the dithiophenol with Ni(II) chloride precursors in toluene solution at ambient temperature as shown in Scheme 2. The compounds have been isolated as purple solids in yields of 88 and 60 % with $\lambda_{\text{max}}$ (thf) for 1 at 511 (v/cm$^{-1}$) 1128, and 2 at 550 (3545) nm. Note that 2 is a kinetic reaction product and was found to gradually convert into a red precipitate of unknown, most likely oligomeric composition. Substituting PCy$_3$ for PPh$_3$ affords a mixture of ill-defined products.

Single crystal XRD structural analysis verified square planar coordination geometries at the trans-dithiolatonickel(II) centres with average Ni-S bond lengths of 2.249(4) and 2.241(2) Å for 1 and 2 which compare well with Ni-S bond lengths reported for structurally related complexes. The molecular structure of 2 is depicted in Figure 1. While two PMe$_3$ donors complete the ligand shell of Ni(II) in 1, use of the more bulky PCy$_3$ ($\Delta\Theta_{\text{trans}} = 52^\circ$) ligand in 2 allows for binding just one phosphine ligand, with a Ni-P bond distance of 2.353(2) Å, and enforces $\eta^2$-coordination of the central aryl ring with averaged Ni-C distances of 2.285(4) Å.

Also in the case of 1 the nickel ion resides above one of the C$_2$H$_2$ edges of the central arene ring, but the average Ni-C distance of 2.614(2) Å is significantly longer, as expected. The molecular structure of 1 is shown in Figure S9, ESI†. Low-temperature $^{13}$C$^1$H and $^1$H NMR data are consistent with $\eta^2$-arene bonding to Ni(II) in 2. At 193 K in d$_2$-CH$_2$Cl$_2$ solution, characteristic resonances of a C$_6$ symmetric structure were observed at 108.4, broadened due to unresolved $^2J_{\text{C,P}}$ coupling, and 8.21 as well as 127.4 and 7.44 ppm which account for the Ni-bound and unbound, yet slowly exchanging C$_2$H$_2$ edges of the central aryl ring as defined in Scheme 2.

Binuclear complexes 3-5 have been isolated in the form of distinct coordination isomers as depicted in Scheme 3 in yields of 51 (3, brown), 75 (4, yellow), and 73 % (5, green) with $\lambda_{\text{max}}$ (thf)nm 3, 520 (v/cm$^{-1}$) 2044, 4, 352 (3005), and 5, 450 (7821). Additional weak absorption bands were detected for each of the dinickel complexes at wavelengths 940-990 nm (v/cm$^{-1}$) 200-500.

Single crystal XRD structure analysis verified the binding modes of the dinickel cores to the dithiophenolate ligand as exemplified for 3 and 5 in Figure 2. A distinct structural feature of 3 is the boat shaped conformation of the central π-system which is present in both the solid state and solution. The variation of bond lengths and deformation from planarity indicate the formation of a syn-$\mu$-$\eta^1$-$\eta^1$ bonding motif, which likely results from significant overlap of the occupied d-orbitals at both nickel ions with a π*-orbital of the arene π-system. Short distances of 1.949(4), 2.035(4), and 2.149(4) Å between Ni and o-, i-, and m- C atoms, and a long Ni-Ni separation of 2.659(1) Å support this description. Observed $\kappa^1$-S-Ni bond lengths of 2.205(1) and 2.193(3) Å compare well with those in literature. Such tight Ni$_2$-arene bonding likely is a consequence of strong charge donation from the thiolate and phosphine ligands to nickel. A structurally similar conformation was reported for the central π-system of a 4-terphenyldithiophosphate ligand that stabilises a bridging $\mu$-$\eta^1$-$\eta^1$-o,o'-biphenyldiol dinickel fragment.
The geometry at each Ni ion may be best described as distorted square planar defined by the sulphur, phosphorous, and the peripheral C-atoms of the η²-allyl moiety. The shortest distance between hydrogen atoms at the PMe₅ ligands is 2.5 Å.

The dinickel core of 3 is dynamic. For an 11.7 T magnetic field, the resonance at δNi 5.41 ppm of protons 8/9-H at the central Ni(I) system was observed to coalesce at 203 K. Further cooling to 178 K gave rise to broad 1H NMR resonances at 4.97 (νNi ~26 Hz) and 5.59 (νNi ~23 Hz) as well as 109 (i-C, νNi ~42 Hz), 74.2 (o-C, νNi ~60 Hz), and 98.5 (m-C, νNi ~55 Hz) ppm. Exchange cross peaks between protons 8/9-H are well resolved. Exchange averaged singlet 1H NMR resonances of the C₂H₅ moieties of the central aryl rings in 4 and 5 have been observed at 8.41 (υNi ~95 Hz) and 7.72 (υNi ~33 Hz) ppm at 168 K. Whether or not this exchange involves preliminary dissociation of one phosphine ligand is unclear albeit no spectral differences have been observed in the presence of excess (≤ 5%) phosphine. As for 3, the apparent exchange of the C₂H₅ sites requires an overall a seesaw-like motion as schematised in Figure 3.

**Computational study**

Comparison of Ni-Ni and Ni-C(arene) bond lengths calculated from single crystal X-ray diffraction data suggests a higher contribution of direct metal-metal (M-M) bonding to the coupling of the nickel ions in case of the syn-endo-Ni₃(μ-S)₂ structural motif in 4 and 5 than in 3. To gain deeper insight into the nature and actual strength of Ni-Ni bonding in these structurally different complexes, we carried out a topological analysis of their electron density distribution, ρ(r), as derived from the DFT calculations on 3 and 5, using the “quantum theory of atoms in molecules” (QTAIM) approach. DFT calculations were performed using GAUSSIAN at the B3LYP/6-311G(d,p) level with dispersion corrections, including Becke-Johnson damping, and substituting the 'Bu groups on the ligand for CH₃ in the theoretical model systems. The optimised geometries were in excellent agreement with the experimental counterparts, the Ni-Ni distances differed by 2 and 6.1 pm for 3 and 5, respectively. For computational details and the full geometries, see the ESI†.

Although numerous experimental and theoretical electron density studies on M-M bonding in dinuclear complexes have been reported, a fundamental understanding of this interaction remains elusive. In both 3 and 5, a stable bond path between the two nickel ions could be identified which implies direct M-M interactions in both systems. This observation is noteworthy, as the presence of bridging ligands usually results in the loss of M-M bond paths, in particular for metal atoms linked by formal single bonds, as concluded by Farrugia and Macchi in a recent review. The topological parameters of ρ(r) at the Ni−Ni bond critical points (BCPs) in 3 and 5 are listed in Table 1, and extended topological data and the molecular graphs of 3 and 5 are provided in the ESI†.

**Table 1.** Selected topological properties at the Ni-Ni bond critical points in the model systems of 3 and 5.

<table>
<thead>
<tr>
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<th>d²</th>
<th>ρ(r)³</th>
<th>V²ρ(r)²ρ(r)²</th>
<th>ε</th>
<th>G(ρ(r))/ρ(r)²</th>
<th>H(ρ(r))/ρ(r)²</th>
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<tr>
<td>3</td>
<td>2.639</td>
<td>0.194</td>
<td>1.856</td>
<td>0.02</td>
<td>0.879</td>
<td>-0.041</td>
</tr>
<tr>
<td>5</td>
<td>2.532</td>
<td>0.407</td>
<td>1.686</td>
<td>0.36</td>
<td>0.674</td>
<td>-0.156</td>
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*Results in Å², *In units of Å³, *In units of e Å³, *In units of hartree Å³.
In both systems, the value for \( \rho(r_{ij}) \) is relatively small, a feature commonly observed for M-M bonds which has been attributed to the diffuse nature of this interaction.\(^{53, 56} \) The slightly negative values for the total energy density, \( H(r_{ij}) \), imply that the potential energy density at these BCPs is somewhat larger than the kinetic energy density which is indicative of covalent bonding, despite the positive value for the Laplacian of \( \rho(r_{ij}) \), \( \nabla^2 \rho(r_{ij}) \).\(^{57} \) A better metric than \( \rho(r_{ij}) \) to assess the actual strength of metal-metal bonding is provided by the delocalization index, \( \delta(A-B) \), which measures the number of electron pairs shared between two atoms A and B, irrespective of existing bond paths.\(^{53, 56, 58} \) For 3 and 5, the values of \( \delta(Ni-Ni) \) equal 0.225 and 0.548, respectively. These smaller, fractional bond orders indicate what has been termed a partial covalent character for formally M-M single bonds, in the sense that not a whole pair of electrons is involved in direct interactions between the atoms.\(^{53} \)

To summarise, the bonding between the Ni atoms in both 3 and 5 can be described as a combination of through-ligand and direct M-M bonding. The latter contribution was clearly identified through the existence of Ni-Ni bond paths. The large increase in the Ni-Ni separation by 27.6 pm [DFT: 31.7 pm] in 3 compared to 5 also reflects a significant reduction of Ni-Ni bond strength: the respective value of \( \delta(Ni-Ni) \) in 5 is more than 2.4 times higher than the one in 3, which can therefore be classified as a bimetallic complex exhibiting only very weak Ni-Ni interactions.

Solution properties of 3-5

VT \(^1\)H NMR data of 3 and 5 revealed a marked dependence of chemical shifts and line-widths of specific proton resonances with temperature and solvent polarity. In case of 3, substituting the solvent \( d_8\)-thf for \( d_6\)-C\(_6\)H\(_6\) at 299 K resulted in a \( \Delta \delta_C \) of +1 ppm for protons 8/9-H at the central \( z \)-system. As shown in Figure 4, variation of the temperature of a \( d_8\)-thf solution of 3 results in a reversible, non-linear variation of \( \Delta \delta_C \) between 5.39 at 198 K and 11 ppm at 405 K, \( \Delta \delta_C(8/9-H) = 5.61 \) ppm.

![Fig. 4](image)

In comparison, observed chemical shift changes for the protons at the flanking phenyl rings, \( \Delta \delta(3-H) = 0.42 \), and 0.88 (5-H) ppm, and for the PMe\(_3\) ligands (0.58 ppm) are smaller by about one order of magnitude but vary in the same non-linear fashion. The largest shift difference in the latter series accounts for the protons most distant from the nickel ions (5-H; for numbering cf. to Scheme 3) whereas resonances of the mesityl (26-H) and \( ' \)Bu substituents are unaffected.

A similarly marked dependence emerged for 5 in \( d_8\)-thf with \( \Delta \delta_C(8,9-H) = 4.94 \) ppm and \( \Delta \delta_C(8,9-H) = 10.12 \) ppm (12.01 ppm in \( d_6\)-C\(_6\)H\(_6\) and \( d_6\)-toluene) whereas it was found to be small in case of 4, with \( \Delta \delta_C(8,9-H) = 0.51 \) ppm and \( \Delta \delta_C(8,9-H) = 8.69 \) ppm. Plots of \( \Delta \delta_C \) vs. temperature for selected types of protons for complexes 4 and 5 are provided in Figures S7-8, ESI†. Respective values of \( \Delta \delta_C \) and the variation with temperature have been observed for both raw products and singly as well as doubly recrystallized samples of 3-5 that were obtained from different batches. This indicates that putative Ni(I) impurities most likely are not the reason for this solution behaviour.

Whereas the \(^1\)H and \(^{13}\)C NMR chemical shifts determined at low temperatures account for the respective structural features observed in the solid state structures of 3-5, the continuous shift of \( \Delta \delta_C \) to lower fields at higher temperatures, especially \( \Delta \delta_C(8/9-H) \) being progressively greater than 11 ppm, suggests thermal population of a paramagnetic biradical (\( S = 1 \)) state\(^9 \) which would add contact and dipolar shift contributions to the observed chemical shift.\(^{28, 59, 60} \) An independent parameter to probe for variable net electron spin moments is the trend of the temperature dependence of the \(^1\)H spin-lattice relaxation time, \( T_1 \), which is expected to be positive for protons in diamagnetic environments. Values of \( T_1 \) for 8/9-H of 3-5 were found to decrease markedly with increasing temperatures, \( e.g. \) \( T_1(8/9-H) \) for 3 in \( d_8\)-thf decreased from 1300 ms at 223K to 110 ms at 323K; \( cf. \) to Figures S3-6, ESI†. Surprisingly, invariable effective magnetic moments of 0.9 B.M. for 3 and 1.0 B.M. for 5 in both toluene and thf solution were determined by Evan’s method\(^{61, 62} \) over the same temperature range at a field of 11.7 T. This finding challenges the hypothesis of the thermal equilibrium population of a paramagnetic spin state. Heating a solution of 5 in \( d_8\)-toluene to 373 K for 3 h was found to slightly increase the effective magnetic moment by \( \sim 0.1 \) B.M. but did not have any effect on the temperature dependence of \( \Delta \delta_C \).

Chemical properties of dinickel cores.

Compounds 3-5 displayed appreciable thermal stability in VT NMR spectroscopic studies of their toluene and thf solutions. While heating a solution of 3 in \( d_8\)-benzene to 343 K for 2 h resulted in low conversion, \( \sim 3 \) %, back into I no changes were observed in \( d_8\)-thf under identical conditions. When dissolved in \( d_8\)-CH\(_2\)Cl\(_2\) at ambient conditions gradual deterioration to yet unknown products occurs in all cases. To gain a more detailed insight into the chemical properties of these bimetallic systems the reactivity of 3-5 was studied qualitatively toward methyl isocyannide (CNCH\(_3\) = L’) by VT NMR spectroscopy.

\(^1\)H and \(^{31}\)P NMR spectroscopic monitoring showed that 5 (\( \delta_H \) 68 ppm) reacts with L’ in a 1:2 stoichiometry at \( T \leq 213 \) K to produce a single product 5*2L’ with characteristic resonances \( \delta_L(Ni-L’) = 2.10 \) and \( \delta_H 22.51 \) ppm as described in Scheme 4.
Coordination of both PPh$_3$ and L' to both Ni sites is supported by $^1$H-$^1$H COSY and $^1$H-$^{31}$P HSQC data which established the presence of scalar $J_{\text{HH}}$ and $J_{\text{HP}}$ coupling of the methyl protons of L' with the o- and m-$^1$H and $^{31}$P nuclei of coordinate PPh$_3$.

Albeit we cannot assign a molecular structure based on the NMR data available, 5*2L' must be a bimetallic complex. Warming the sample to 263 K in the NMR probe resulted in the progressive formation of (Ph$_3$P)$_2$(L')(Ni(0)) at the expense of the resonances of 5*2L', with characteristic $^1$H and $^{31}$P NMR resonances at 2.85 ppm (N-line pattern, L') and $\delta_{P}$ 33.2 ppm. The identity of this Ni(0) product has been established unequivocally through independent synthesis from Ni(COD)$_2$, 2 equiv. of PPh$_3$ and L' in an NMR tube reaction under otherwise identical conditions.

Scheme 4. Reactivity of binuclear 5 toward CNCH$_3$(L') monitored in situ by VT NMR spectroscopy in d$_8$-thf ($\delta_{\text{N}}$ucleus in ppm at 11.7 T).

IR spectra taken with a dip probe at 193K showed the appearance of an intense band at 2051 cm$^{-1}$, along with a weak band at 2152 cm$^{-1}$, for 5*2L' whose intensity reached a maximum after the addition of 2 equiv. of L'. As expected, both bands disappeared upon warming the solution to room temperature due to the disproportionation of 5*2L', and were replaced by broad bands at 2109 and 2060 cm$^{-1}$. These bands compare well with literature reported values for complexes of the type (Ph$_3$P)$_n$(RNC)$_{4-n}$Ni(0), with $n$ = 1-3, and R = 'Bu, Cy, and PhCH$_2$.

In clear contrast, addition of 1 equiv. of L' to 3 at 213 K afforded an asymmetric compound which we assign as 6 shown in Scheme 5. The complete assignment of $^1$H and $^{31}$P NMR data of putative 6 is given in the ESI†. The PMe$_3$ ligands in 6 are non-equivalent but appear to coordinate to the same nickel site, with $^3J_{\text{PP}}$ = [54] Hz. The magnitude of $^3J_{\text{PP}}$ of the putative isomeric structure 6$_{\text{iso}}$ may be expected to be significantly smaller if detectable at all. Selective $^{31}$P decoupling of $^1$H NMR data aided in the assignment of the two PMe$_3$ ligands. Both phosphine ligands showed $^1$H-$^1$H NOE contacts to L' ($\delta_{\text{H}}$ 3.32 ppm), which would not have been possible if PMe$_3$ and L' were coordinating in trans-fashion to the same nickel ion as in 6$_{\text{iso}}$. Ni-arene d-$\pi^*$ back bonding appears to be insignificant, judging from the chemical shifts of the four distinct resonances of the central ring protons, $\delta_{\text{H}}$ being 7.74, 6.53, 6.47, and 6.18 ppm at 193 K. The central $\pi$-system of the 4-terphenyl backbone may act as a $\sigma$-donor to complete the ligand shell at the Ni-L' site as indicated in Scheme 5. As observed for complex 2, the shift of one of the above $^1$H resonances to lower field may reflect dative bonding of the $\pi$-system to nickel which binds another strong $\sigma$-donor ligand such as PCy$_3$ and L' in trans-position.

Scheme 5. Reactivity of 3 toward CNCH$_3$(L') monitored by in situ VT NMR spectroscopy (L = PMe$_3$, R' = 2,4,6-(H$_3$C)$_3$C$_6$H$_2$, R = 'Bu). Dashed line accounts for the capability of L' to $\mu$-bonding.
The structure of 6 is dynamic in solution. Exchange spectra show that the PMe₃ ligands slowly exchange Ni sites with L’ at 213 K, see Figures S1-2 in the ESI†. The known capability of L’ to coordinate in μ-fashion¹⁹, ⁶⁵ likely triggers this exchange process as indicated in Scheme 5.

Monitoring the addition of L’ to 3 at 193 K in thf by IR spectroscopy showed gradual appearance of a broad band at 2064 cm⁻¹, along with a significantly weaker broad band centred at 2124 cm⁻¹. Bands at wavenumbers greater than 2000 cm⁻¹ have been reported as characteristic for terminal rather than bridging coordination of isocyanide ligands in bimetallic complexes of low-valent nickel.¹⁹, ⁶⁵ Compared to a reference sample with no added 3, L’ coordination results in a shift of the C≡N stretching mode by 100 cm⁻¹ to lower energy, indicating significant d-π* charge transfer from Ni to L’. At 234 K, ¹H NMR resonances of the central arene ring protons are subject to exchange broadening and resonances of 1 began to gradually grow into the spectra. The addition of two equivalents of L’ to 3 resulted in complete conversion of 6 into 1. IR spectra taken at the same temperatures showed a broad band centred at 1855 cm⁻¹ that irreversibly formed at the expense of the bands at 2124 and 2064 cm⁻¹ that had originally been observed upon L’ addition at 193K.

Conclusions

Mono- and binuclear complexes of Ni(I) have been prepared from a 4-terphenyldithiophenol ligand. Steric interactions between phosphine and substituents at the 4-terphenyl backbone result in the formation of coordination isomeric structures with thiolate bonding either in bridging or terminal fashion. In the latter case, significant d-π* charge transfer causes the 4-terphenyl ligand backbone to coordinate to the Ni ions in a syn-μ-S₃-N₃ fashion. Electronic coupling of metal centres within the Ni₂(μ-S)₂ core displayed in 4 and 5 involves bonding interactions via the bridging thiolates but also direct M-M bonding with calculated δ(Ni-Ni) = 0.548, whereas a delocalisation index of 0.225 indicates significantly weaker coupling of the Ni(I) ions in 3. The origin of the chemical shift dependence on temperature observed for 3-5 is currently not understood but most likely reflects changes of the electronic properties of the bimetallic core. Whereas metal-thiolate bonding couples protons 3/5-H to the Ni ions, 8/9-H at the central π-system bind directly to the latter. Albeit plausible this hypothesis necessitates further studies.

Coordination of a π-acceptor ligand such as methyl isocyanide to 3 and 5 subjects the bimetallic fragments to disproportionation. Interestingly, the nature of the phosphine ligand determines the character of intermediately formed species and the temperature at which Ni(0) species are extruded. The binuclear Ni₂(μ-S)₂ structure in 5 persists upon binding of 2 equiv. of isocyanide at low temperatures. In case of 3, apparent PMe₃ migration to the same nickel site is triggered by isocyanide bonding. This structural reorganisation reaction is remarkably facile even at low temperature which may be a consequence of the weak electronic coupling of the Ni ions, as also reflected by the calculated delocalisation index from solid state structural data. The magnitude of metal-metal electronic coupling may be taken as a parameter which determines the electronic flexibility and thus reactivity of bimetallic structures.⁶⁶ The bimetallic complexes of nickel described herein provide a complementary set of model compounds suitable for studies on the structural effects on the reactivity of binuclear systems toward electrophilic reactants.

Experimental

General considerations.

All reactions were carried out under a dry argon atmosphere using standard Schlenk or glove box techniques (MBraun, MB 150-G1). All solvents were purified and dried prior to use. Dichloromethane and hexane were dried over Grubbs columns of an MBraun solvent purification system. Benzene, diethyl ether, pentane, tetrahydrofuran, and toluene were pre-dried over activated 3 Å molecular sieves and distilled from sodium benzophenone ketyl or potassium metal under argon. Methanol was dried over activated neutral alumina. d₆-Benzene, d₆-toluene, and d₆-thf were dried over and distilled from NaK alloy whereas d-CHCl₃ and d₆-CH₂Cl₂ were dried over and vacuum transferred from 3 Å molecular sieves. All solvents were stored over 3 Å molecular sieves under argon. Molecular sieves and neutral alumina were activated by heating under dynamic vacuum (10⁻³ mbar) at 250 °C for 24-48 hours. UV-Vis spectra were collected on a PerkinElmer Lambda 35 spectrophotometer. The range from 200 to 1100 nm was scanned at a speed of 480 nm per minute, using 1 cm quartz cuvettes sealed with Teflon stoppers. Combustion analyses were performed on an Elementar Vario MICRO instrument. NMR data were recorded on Bruker Avance II 400 and DRX 250 instruments. VT NMR spectra were collected on a Bruker AVIII+500 spectrometer. δ values are given in ppm, J values in Hz. ¹H and ³¹P NMR chemical shifts are referenced to the residual proton and naturally abundant carbon resonances of the solvents: 7.16/128.06 (d₆-C₆H₆), 1.72/67.21 (d₆-thf), 5.32/53.84 (d₆-CH₂Cl₂), and 7.26/77.16 (d-CHCl₃) ppm. ³¹P NMR chemical shifts are referenced to an external standard sample of 85% H₃PO₄ set to 0 ppm. VT solution IR spectra were taken with a Mettler Toledo ReactIR 15 system equipped with a Sicomp dip probe at a spectral range from 2600 to 650 cm⁻¹. Ligand preparation is described in the ESI†. The compounds (Me₂P)₂NiCl₂, Ni(COD)₂, (Ph₃P)₂NiN(SiMe₃)₂, (pyridine)NiCl₂, and methyl isocyanide were prepared following procedures adapted from literature. Caution: Methyl isocyanide is toxic and has a very unpleasant odour. All manipulations with this reagent should be carried out in a fume hood. X-ray data were collected on a Bruker Smart APEX II diffractometer with graphite-monochromated Mo Kα radiation. The programs used were Bruker’s APEX2 v2011.8-0, including SADABS for absorption correction and SAINT for structure solution, the WinGX suite of programs version 2013.²³
SHELXS for structure solution, SHELXL for structure refinement\textsuperscript{76, 77} and PLATON.\textsuperscript{76} Crystals were, unless otherwise noted, coated in a perfluoropolyether oil and mounted on a 100 μm MiTeGen MicroMounts\textsuperscript{74} loop that was placed on the goniometer head under a stream of dry nitrogen at 100 K.

**Preparation and characterization of 1.**

Ligand (500 mg, 0.776 mmol), benzylic potassium (210 mg, 1.550 mmol), and toluene (40 mL) were combined in a Schlenk flask. The resulting mixture was stirred for 0.5 hours (h) at r.t. to form a yellow solution. After this time, (Me₂P)₂NiCl₂ (220 mg, 0.780 mmol) was added and stirring was continued for an additional 2 h at r.t. The solution gradually turned dark purple and a white solid separated. The solution was filtered off, the solvent removed under vacuum, and the residual dark purple solid repeatedly (3x) washed with 10 mL portions of pentane vapour into a concentrated solution of I in benzene produced single crystals also suitable for XRD analysis.

δ₁ (400 MHz; d₄-C₆H₄Cl): 298 K 7.76 (2 H, d, J = 2.4, 4, 3-, 18-H), 7.56 (4 H, s, 8-, 9-, 11-, 12-H), 7.05 (2 H, d, J = 2.6, 4, 5-, 16-H), 6.95 (4 H, s, 21-, 23-, 32-, 34-H), 2.29 (12 H, s, 25-, 27-, 36-, 38-H), 2.17 (6 H, s, 26-, 37-, 38-H), 1.33 (18 H, s, 4-, and 17- Bu). 0.77 (18 H, N-line pattern 2\textsuperscript{15}J(CH) 7.83, P(CH₃)), δ₂ (100 MHz; d₄-C₆H₄Cl): 298 K 144.22, 143.41, 141.83 (t, J₆-H 2.1, C-1, -14), 141.63 (C-19, -30), 140.75, 140.12, 136.10 (C-20, -24, -31, -35), 135.65 (C-22, -33), 128.36 (C-21, -23, -32, -34), 126.34 (C-5, -16), 123.85 (C-8, -9, -11, -12), 122.77 (C-3, -18), 34.19 (C-28, -40), 31.63 (C-29, -39), 21.19 (C-26, -37), 20.97 (C-25, -27, -36, -38), 12.47 (N-line pattern 2\textsuperscript{13}J(C₆H₃) 27.7, P(CH₃)).

δ₃ (162 MHz; d₄-C₆H₄Cl): 298 K -27.98 (Ni-CH₃). Elemental analysis found: C, H, S. 6.73%. Calc. for C₉H₆N₂P₂: 2CHCl₃: C, 68.18; H, 8.16; S, 7.00%. UV-Vis: λ_max (thf)/nm 257 (ε/dm\textsuperscript{3}mol\textsuperscript{-1}cm\textsuperscript{-1}) 67671, 280 (52736), 351 (13220) and 511 (1128).

Crystal data: C₉H₆N₂P₂: 2CH₂OH, M = 915.88, monoclinic, a = 13.5105(2), b = 12.1898(2), c = 29.9385(5) Å, U = 4928.25(14) Å\textsuperscript{3}, T = 100(2) K, space group P1 21/c, Z = 4, 27715 reflections measured, 10728 unique (R_int = 0.0223) which were used in all calculations. The final wR(F₂) was 0.1114 (all data).

**Preparation and characterization of 2.**

Ligand (500 mg, 0.776 mmol), benzylic potassium (210 mg, 1.550 mmol), and toluene (40 mL) were combined in a Schlenk flask. The resulting mixture was stirred for 30 minutes at r.t. to form a yellow solution. After (pyridine)NiCl₂ (360 mg, 0.776 mmol) and tricyclohexylphosphine (210 mg, 0.776 mmol) were added, stirring was continued for an additional 2 h at r.t. The solution turned brown and a white solid separated. After filtration, the solvent removed under vacuum, the residual brown solid repeatedly (3x) washed with 10 mL portions of methanol, and dried under dynamic vacuum to produce solid dark purple 2 (456 mg, 60%). Crystallisation by slow diffusion of pentane vapour into a concentrated solution of 2 in thf produced single crystals suitable for XRD analysis.

δ₁ (500 MHz; d₂-CH₂Cl₂): 273 K 7.76 (4 H, s, 8-, 9-, 11-, 12-H), 7.27 (2 H, d, J₅-J₃ 2.3, 4, 5-, 18-H), 6.78 (4 H, s, 21-, 23-, 32-, 34-H), 6.73 (2 H, d, J₅-J₃ 2.3, 4, 5-, 16-H), 2.19 (6 H, s, 26-, 37-H), 1.91 (12 H, s, 25-, 27-, 36-, 38-H), 1.27 (18 H, s, 4-, and 17-Bu). 2.04-0.75 (m, P(CH₃)₃).

δ₂ (126 MHz; d₂-CH₂Cl₂): 273 K 146.25 (C-4, -17), 141.72 (C-6, -15), 141.02 (C-19, -30), 140.71 (C-2, -13), 139.60 (C-7, -10), 137.93 (C-1, -14), 136.07 (C-20, -24, -31, -35), 135.88 (C-22, -33), 128.08 (C-21, -23, -32, -34), 127.59 (C-5, -16), 121.49 (C-3, -18), 118.62 (C-8, -9, -11, -12), 34.56 (C-28, -40), 33.53 (d, P(CH₃)₃), 31.42 (C-29, -39), 30.11 (d, P(CH₃)₃), 27.19 (d, P(CH₃)₃), 26.82 (d, P(CH₃)₃), 21.15 (C-26, -37), 20.88 (C-25, -27, -36, -38).

δ₃ (162 MHz; d₂-CH₂Cl₂): 273 K 15.42. Elemental analysis found: C, 74.32; H, 8.44; S, 6.27. Calc. for C₉H₆N₂P₂: C, 75.98; H, 8.33; S, 6.54%.
UV-Vis: \( \lambda_{\text{max}} \) (thf)/nm 253 (\( \varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1} \)) 28630), 269 (27354), 283 (24012), 298 (21892), 453 (4545) and 550 (3545). Crystal data: C_{2}H_{3}NiPS_{2}, C_{6}H_{4}O, M = 1052.17, monoclinic, \( a = 9.7947(5) \), \( b = 31.5469(16) \), \( c = 19.7427(11) \) Å, \( U = 6084.0(6) \) Å\(^3\), \( T = 100(2) \) K, space group P1 21/n, \( Z = 4 \), 81481 reflections measured, 12065 unique (\( R_{\text{int}} = 0.0491 \)) which were used in all calculations. The final \( wR(F_{2}) \) was 0.2111 (all data).

Preparation and characterization of 4.

Compound 2 (100 mg, 0.102 mmol), Ni(COD)$_2$ (28 mg, 0.102 mmol), tricyclohexylphosphine (29 mg, 0.103 mmol), and thf (25 mL) were combined in a Schlenk flask. The resulting mixture was stirred for 2 h at r.t. to form a yellow solution. After removing the solvent under dynamic vacuum, the residual yellow solid was repeatedly (3x) washed with 5 mL portions of pentane, and dried under dynamic vacuum to produce solid yellow 4 (80 mg, 75%). Bulk crystallisation by slow diffusion of pentane layered on top a concentrated thf solution produced single crystals suitable for XRD analysis. \( \delta_{\text{H}} \) (500 MHz, d$_6$-thf, 253 K) 8.59 (4 H, br s, 8-, 9-, 11-, 12-H), 7.35 (2 H, d, 15.3, 2.3, 3., 18-H), 6.81 (2 H, d, 15.5, 2.2, 4., 5., 16-H), 6.74 (4 H, s, 21-, 23-, 32-, 34-H), 2.23 (6 H, s, 26-, 27-H), 1.94 (12 H, s, 25-, 27-, 36-, 38-H), 1.30 (18 H, s, 4-, and 17-Bu), 2.05-0.72 (PCy$_3$).

Elemental analysis found: C, 72.28; H, 8.74; S, 5.00%. Calc. for C$_{50}$H$_{38}$S$_2$: C, 74.90; H, 6.13; S, 5.00%.

UV-Vis: \( \lambda_{\text{max}} \) (thf)/nm 315 (\( \varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1} \)) 23050, 380 (17718), 450 (7821), 725 (576) and 990 (527). Crystal data: C$_{10}$H$_{22}$Ni$_2$P$_4$S$_2$, M = 1282.9, triclinic, \( a = 11.9127(3), \) b = 21.1860(5), c = 28.2328(7) Å, \( T = 100(2) \) K, space group P-1, Z = 2, 51911 reflections measured, 17549 unique (\( R_{\text{int}} = 0.0224 \)) which were used in all calculations. The final \( wR(F_{2}) \) was 0.1013 (all data).

Preparation and characterization of 5.

To a yellow solution of (Ph$_2$P)$_2$NiNi(SiMe$_3$)$_2$ (463 mg, 0.622 mmol) in thf (50 mL) was added a solution of ligand (200 mg, 0.311 mmol) in thf (5 mL) water, and the resulting mixture stirred for 2 h at r.t. The solution gradually turned dark green. After removing the solvent under dynamic vacuum, the residual green solid was repeatedly (3x) washed with 10 mL portions of pentane, and dried under dynamic vacuum to produce solid 5 (215 mg). The raw product contains additional PPh$_3$, typically ≤ 5%, as the only impurity. NMR spectroscopic properties of raw products are identical to samples recovered after one and two recrystallization steps. Recrystallization was performed by slow vapour diffusion of pentane, or hexane, into a concentrated solution of 5 in thf and produced green single crystals which were also suitable for XRD analysis (155 mg 39%). Other than the co-crystallized hydrocarbon, the material contains varying amounts of trapped thf, rendering elemental analysis difficult. \( \delta_{\text{H}} \) (500 MHz, d$_6$-C$_6$H$_6$, 299 K) 12.01 (4 H, br s, 8-, 9-, 11-, 12-H), 7.99 (2 H, d, 15.3, 1.6, 4., 3., 18-H), 7.86 (2 H, d, 15.5, 1.8, 4., 5.-, 16-H), 7.48 (m, PPh$_3$), 7.02 (m, PPh$_3$), 6.84 (m, PPh$_3$), 6.78 (4 H, s, 21-, 23-, 32-, 34-H), 2.28 (6 H, s, 26-, 37-H), 1.68 (12 H, s, 25-, 27-, 36-, 38-H), 1.22 (18 H, s, 4-, and 17-Bu).

\( \delta_{\text{C}} \) (126 MHz, d$_6$-C$_6$H$_6$, 299 K) 164.71, 152.34, 142.79, 136.41, 136.37, 135.04, 133.79, 129.48, 126.01, 115.33, 33.20, 32.25, 21.27, 20.73.

UV-Vis: \( \lambda_{\text{max}} \) (thf)/nm 10.12 (4 H, br s, 8-, 9-, 11-, 12-H), 7.53 (2 H, d, 15.5, 2.2, 4., 3., 18-H), 7.36 (2 H, d, 15.5, 2.3, 4., 5., 16-H), 7.29 (m, PPh$_3$), 7.17 (m, PPh$_3$), 6.55 (4 H, s, 21-, 23-, 32-, 34-H), 2.26 (6 H, s, 26-, 37-H), 1.36 (18 H, s, 4-, and 17'-Bu), 1.26 (12 H, s, 25-, 27-, 36-, 38-H).

\( \delta_{\text{C}} \) (126 MHz, d$_6$-thf, 298 K) 159.11, 150.80 (C-4, -17), 147.85, 142.56 (C-19, -30), 137.45, 137.09 (PPh$_3$), 136.05, 135.47 (PPh$_3$), 130.58 (C-8, -9, -11, -12), 130.09 (PPh$_3$), 129.24, 128.80 (PPh$_3$), 128.23 (C-21, -23, -32, -34), 127.73 (C-5, -16), 125.60 (C-1, -14), 124.93 (C-3, -18), 34.57 (C-28, -40), 32.39 (C-29, -39), 21.60 (C-25, -27, -36, -38), 21.10 (C-26, -37).

\( \delta_{\text{C}} \) (202 MHz, d$_6$-thf, 213 K) 68 (\( \nu_{\text{C}} \approx 800 \) Hz).

Elemental analysis found: C, 73.84; H, 6.22; S, 4.87. Calc. for C$_{50}$H$_{38}$S$_2$: C, 74.90; H, 6.13; S, 5.00%.

Computational details

DFT calculations on 3 and 5 were performed with the GAUSSIAN 09 program suite\textsuperscript{42}, using the B3LYP density functional\textsuperscript{43-45}, along with the implemented 6-311G(d,p) basis set\textsuperscript{46-49} and dispersion corrections, including Becke-Johnson damping.\textsuperscript{50, 51} For the theoretical model systems, the 'Bu substituents on the bridging 4-terphenyldithiophenolate ligand were replaced by methyl groups. All geometry optimizations were initially carried out without imposing any symmetry constraints. The geometry of 3, however, converged close to C$_2$ symmetry and was subsequently optimised within this symmetry. All geometrical parameters were in excellent agreement with their experimental counterparts. The optimized structures were confirmed as true minima on the respective potential energy surface by calculating analytical frequencies. Modes with imaginary frequencies were absent for both 3 and 5. The topology of the electron density was analysed using the software package AIMALL.\textsuperscript{41} Plots were generated using AIMALL and CHEMCRAFT.\textsuperscript{77}

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Notes and references

The BCP represents the point of minimum electron density, $\rho(r)$, along the bond path between two atoms, in which $\rho(r)$ is locally greater than in any direction away from the path.
The preparation and characterisation of binuclear Ni(I) complexes from a 4-terphenyldithiophenol ligand is described.

\[ \text{Delocalisation index } \alpha(\text{Ni-Ni}): \begin{array}{cc} 0.225 & 0.548 \end{array} \]