Stereodiscrimination in Phosphanylthiolato Nickel(II) Complexes

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The presence of a stereogenic carbon centre (*R* or *S*) in the racemic ligand 1-(diphenylphosphanyl)propane-2-thiol induces a conformational preference (λ or δ) in the five-membered chelate ring of its 2:1 and 2:2 coordination compounds with Ni[II]: the mononuclear *trans*-[Ni{SCH(CH₃)CH₂PPh₂-*P,S*}₂] (**1**) and the binuclear *trans*-[Ni{μ-SCH(CH₃)CH₂PPh₂-*P,S*}(Cl)]₂ (**2**). Both complexes exist as mixtures of two diastereomers: racemic-*trans* (R_λ, R_λ and S_δ, S_δ) and *meso-trans* (R_λ, S_δ), in an equilibrium displaced towards the more stable isomer, the *meso-trans* for **1** (calculated $\Delta E = < -0.1$ kcal·mol⁻¹) and the racemic-*trans* for **2** (calculated $\Delta E = -5.1$ kcal·mol⁻¹). This phenomenon is especially evident for complex **2**, in which an efficient chiral recognition between the two enantiomeric forms of the racemic ligand was observed. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

The reactivity of 2-phosphanylthiolato nickel(II) complexes has been studied because of their relevance in *S*-alkylation/*S*-dealkylation reactions[1] and their applications in desulfurisation technologies[2] and in understanding the biological pathways of certain sulfur-containing metalloproteins.[3] However, less attention has been given to the importance of the ligand-based stereoelectronic effects in determining the coordination conformations around the metal and the stereochemistries of these compounds.[4] Thus, we decided to focus our attention on these particular aspects. The bis(phosphanylthiolato)nickel(II) complexes *trans*-[Ni(SCH₂CH₂PR₂-*P,S*)₂][4,5] exist as mixtures of diastereomers because the five-membered chelate ring can adopt two different conformations (λ and δ) and therefore is able to form three optically isomeric complexes. When both chelate rings are in a λ-conformation, and the two chelate rings of the enantiomer are in a δ-conformation, we have the racemic-*trans* complex and when each chelate ring is in a different conformation, we have the *meso-trans* diastereomer (see Scheme 1). These two stereoisomers can be distinguished when a racemic chiral ligand is present, such as in complex [Ni(SCH₂CH₂PMePh)₂], which has a racemic ligand chiral at the phosphorus centre. This compound exists in solution as a mixture of the racemic-*trans* and the *meso-trans* forms that equilibrate slowly ($t_{1/2}$ ca. 12 h) through an intermolecular process to form a 1:1 mixture, since the two diastereomers have very close energies.[4]
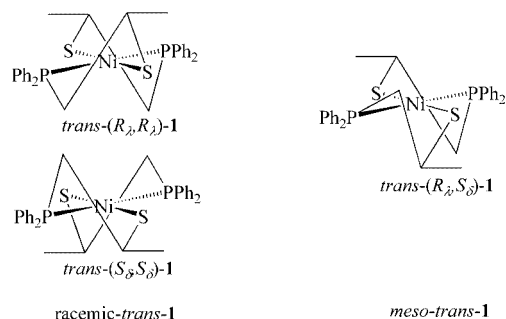
Scheme 1. Stereoisomers of mononuclear five-membered ring bis(phosphanylthiolato)nickel(II) complexes exemplified by complex **1**

The same stereochemical analysis can be applied to the 2-phosphanylthiolato-bridged binuclear nickel(II) complexes [Ni(μ-SCH₂CH₂PR₂)(X)]₂, which form bent *syn-endo-trans* structures.[6,7] Theoretical studies have shown that for this class of compounds the stabilisation of folded structures with respect to the planar arrangement can be

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ascribed to the pyramidalisation of the sulfur bridge compounded with a weak Ni−Ni interaction. Furthermore, it has been proposed that in a bent structure the chelate ring involving the bridging sulfur would be highly strained in *syn-exo* or *anti* conformations.[7] As in the case of bis(phosphanylthiolato) complexes, the chelate chain introduces some degree of structural variation, also producing the racemic-*trans* and *meso-trans* diastereomers (see Scheme 2). Nevertheless, it should be noted that the *anti* conformation of the bridging sulfur substituents would be necessary for the *meso-trans* isomer to be formed and that, for this type of complexes, the bent-*anti* structure has been observed neither in the solid state nor in solution.
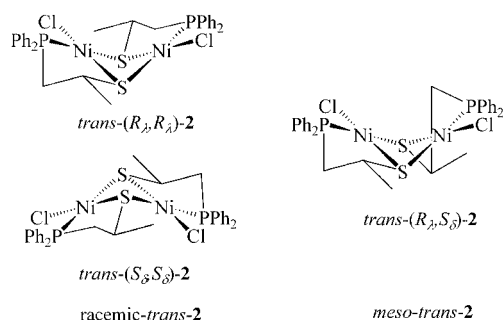
Scheme 2. Stereoisomers of double 2-phosphanylthiolato-bridged binuclear nickel(II) complexes with bent structures exemplified by complex **2**

For these reasons, we propose that the energy difference between the racemic-*trans* and *meso-trans* diastereomers of bis(phosphanylthiolato) complexes, and the strong tendency of the phosphanylthiolato-bridged binuclear complexes to adopt the folded *syn-endo-trans* conformation, could produce a chiral discrimination between the two enantiomeric conformations of the five-membered chelate ring. In order to demonstrate this hypothesis, we synthesised and characterised the 2:1 and 1:1 coordination compounds of the racemic ligand 1-(diphenylphosphanyl)propane-2-thiol[8] with nickel(II).

Results and Discussion

An alternative method to the literature procedures for the syntheses of $[Ni(SCH_2CH_2PPh_2)_2]$[5,9] and $[Ni(\mu\text{-}SCH_2CH_2PPh_2)(Br)]_2$[9] was applied to prepare the mononuclear bis-chelate *trans*-$[Ni\{SCH(CH_3)CH_2PPh_2\}_2]$ (**1**) and the binuclear *trans*-$[Ni(\mu\text{-}SCH(CH_3)CH_2PPh_2)(Cl)]_2$ (**2**) complexes. Addition of a CH_2Cl_2 solution of two equiv. of racemic 1-(diphenylphosphanyl)propane-2-thiol to a solution of nickel chloride in methanol resulted in the formation of solid **1**, which was isolated in 85 % yield. The same base-free procedure was used for **2**, which was isolated in 80 % yield upon addition of one equiv. of the racemic ligand and precipitation with diethyl ether.[10]

The *trans* geometry of the mononuclear complex **1** was determined by NMR analysis. In the $^{13}C\{^1H\}$ NMR spectra all aliphatic carbon atoms appear as triplets owing to virtual coupling with two equivalent mutually *trans* phosphorus nuclei (see Figure 1). According to the $^{31}P\{^1H\}$ NMR spectrum, bis-chelate **1** exists as a mixture of two diastereomers: freshly prepared $CDCl_3$ solutions of complex **1** show two resonances at δ_P = 52.6 and 54.2 ppm in about an 11:5 intensity ratio. The similar δ_P values point to two diastereomers with the same configuration but different conformations.
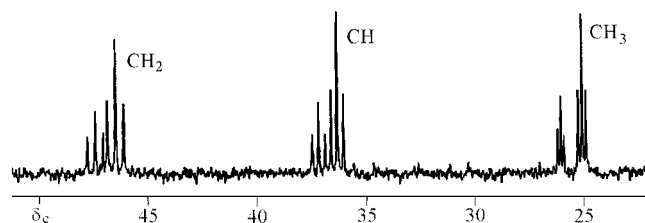

Figure 1. The aliphatic $^{13}C\{^1H\}$ NMR signals of complex **1** appear as triplets owing to virtual coupling with 2 equiv. mutually *trans* phosphorus nuclei

In keeping with the conformational analysis for compound **1** (see Scheme 1), the preferred conformation for the chiral chelate ring depends on the configuration at the stereogenic carbon centre of the ligand.[10a] Thus, the ligand with *R* configuration adopts the λ-conformation, which places the substituent of the chelate ring in the equatorial position. For the same reasons, the ligand with *S* configuration adopts the δ-conformation. As a result of these conformational preferences, complexes carrying two ligands with the same configuration, *trans*-(*R*,*R*)-**1** and *trans*-(*S*,*S*)-**1** are enantiomers (racemic-*trans*-**1**) giving a single $^{31}P\{^1H\}$ NMR signal. The second resonance is then assigned to the diastereomeric complex carrying one ligand in each configuration, *trans*-(*R*,*S*)-**1** (*meso-trans*-**1**). By comparison with the related complex $[Ni(SCH_2CH_2PMePh)_2]$,[4] the major signal could be initially assigned to the racemic-*trans*-**1** stereoisomer, which was claimed to be the kinetic product. However, the intensity ratio of the $^{31}P\{^1H\}$ NMR signals remains constant after 72 h at 50 °C. This behaviour contrasts with that observed for other similar Group VIII metal bis(phosphanylthiolato) complexes, in which the two signals become equal after 24 h at room temperature. In the latter case the two diastereomers have very close energies,[4,10a] suggesting that for complex **1** they have a slight, but significant, difference in energy (experimental $\Delta E \approx$ 0.41 kcal·mol^{-1}). The BP86 energy calculations on complex **1** (see below) reveal that this energy difference is really small (less than 0.1 kcal·mol^{-1}) and predict the stabilisation of the *meso-trans*-**1** isomer over the racemic-*trans*-**1**, owing most probably to the steric interactions between the *pseudo*-axial phenyl groups that are mutually *syn* in racemic-*trans*-**1** and *anti* in *meso-trans*-**1** (see Scheme 3).

Binuclear complex **2** adopts a bent *syn-endo-trans* conformation in the solid state (see below) and shows a single, sharp resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ_P = 36.3 ppm, both for freshly prepared and aged solutions,
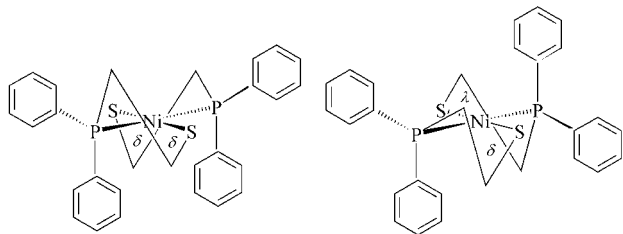
Scheme 3. The pseudo-axial phenyl groups of the *trans*-bis(2-diphenylphosphanylthiolato)nickel(II) complexes are mutually *syn* in the stereoisomers carrying both chelate rings in the same conformation (λ, λ or δ, δ) and *anti* in the stereoisomer with one chelate ring in each conformation (λ, δ)

pointing to the presence of only one of the possible diastereomers. It is noteworthy that in the $^{13}C\{^1H\}$ NMR spectrum of binuclear **2**, two of the aromatic carbon atoms (C_o and C_m) show two signals each, and all are pseudo-triplets (see Figure 2). The doubling of these signals is assigned to the different surroundings of each phenyl ring in the same diphenylphosphanyl group, while the fine splitting could be ascribed to a somewhat surprisingly similar coupling to both phosphorus nuclei generated by the P−Ni−Ni−P connection, a special case of the known phenomenon of virtual coupling.[7]
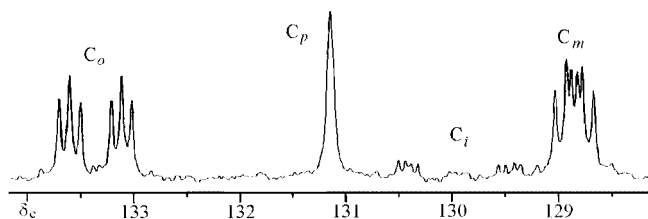

Figure 2. Two of the aromatic $^{13}C\{^1H\}$ NMR signals of complex **2** appear as pseudo-triplets (C_o and C_m), probably owing to a P−Ni−Ni−P coupling; complex **2** is not soluble enough to obtain quality signals for the quaternary carbon atoms, but an unfolded doublet of doublets can be glimpsed in the spectral trace

The conformational analysis of complex **2** shows, as in the case of **1**, that ligands with *R* and *S* configuration adopt λ and δ conformations, respectively, thereby placing the chelate chain substituent in the equatorial position. Thus, two diastereomeric forms of **2** could exist (racemic-*trans*-**2** and *meso*-*trans*-**2**: see Scheme 2), but only one of them was observed in solution. The BP86 energy calculations on complex **2** (see below) gave an energy difference of 5.1 kcal·mol^{-1} between the racemic-*trans*-**2** and the *meso*-*trans*-**2** isomers, in agreement with an equilibrium strongly displaced towards the racemic-*trans*-**2** diastereomer (experimental $\Delta E \geq 2.3$ kcal·mol^{-1}).[11] Furthermore, the minimum in energy for the *meso*-*trans*-**2** isomer represents a folded *syn*-*endo*-*trans* structure with one of the chelate chain substituents in the equatorial position and the other in the axial position. This result is in agreement with the instability of the bent *anti* conformations predicted for this type of complex.[7]

An XRD study was carried out on crystals of **2**·CHCl$_3$ (see Figure 3). The crystal structure contains only the racemic-*trans*-**2** diastereomer and reveals an edge-sharing binuclear complex with square-planar coordination geometry around the nickel atoms. The molecule adopts a folded *syn*-*endo*-*trans* conformation (see Figure 3). Although the Ni−S, Ni−P and Ni−Cl distances are in the range observed for the isostructural [Ni(μ-SCH$_2$CH$_2$PPh$_2$)(X)]$_2$ complexes (where X = Cl, Br), the fold angle of the central four-membered Ni$_2$S$_2$ cycle is appreciably greater (118.1 vs. 100.7−104.1°), increasing the Ni−Ni distance from 2.681−2.695 to 2.906 Å.[6] The reason for this geometrical alteration must be attributed to the presence of the substituent in the chelate chain, because there are no other structural changes. In complex **2**, the requirement to locate the methyl group in the equatorial position increases the bending of the tertiary carbon atom away from the S−S hinge (33.6 vs. 27.1−27.8°) and, since this bending is related to the arching of the Ni$_2$S$_2$ group,[7] the central core must unfold.
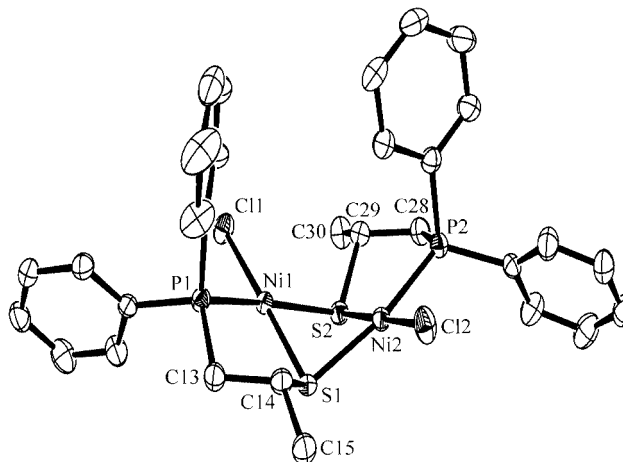

Figure 3. ORTEP plot (50 %) of complex **2**, hydrogen atoms are omitted; selected distances (Å) and angles (°): Ni1−Ni2 2.9065(4), Ni1−S1 2.1556(6), Ni1−S2 2.2244(7), Ni1−P1 2.1705(7), Ni1−Cl1 2.1910(7), Ni2−S1 2.2081(7), Ni2−S2 2.1558(7), Ni2−P2 2.1559(7), Ni2−Cl2 2.1811(7), S1−C14 1.841(3), C13−C14 1.531(4), C14−C15 1.516(4), P1−C13 1.834(3), S2−C29 1.854(3), C28−C29 1.520(4), C29−C30 1.521(4), P2−C28 1.833(3), S1−Ni1−P1 87.99(3), P1−Ni1−Cl1 95.22(3), S1−Ni1−S2 79.51(2), Cl1−Ni−S2 97.74(3), S2−Ni2−P2 88.29(3), P2−Ni2−Cl2 92.58 (3), S2−Ni2−S1 79.81(3), Cl2−Ni2−S1 99.15 (3), Ni1−S1−Ni2 83.52(2), C14−S1−Ni1 105.94(8), C14−S1−Ni2 112.74(9), Ni2−S2−Ni1 83.13(2), C29−S2−Ni2 105.38(8), C29−S2−Ni1 112.77(9).

Computational Results

The reported calculations were carried out by using the Amsterdam density functional (ADF2002.03) program system, developed by Baerends et al.[12−14] The numerical integration scheme employed was that of te Velde and Baerends.[15] An uncontracted triple-ζ basis set[16] was used

for describing the 3s, 3p, 3d, 4s, and 4p orbitals of nickel. For carbon (2s,2p), phosphorus (3s,3p), sulfur (3s,3p), and hydrogen (1s), double-ζ basis sets[16] were employed and augmented by an extra polarisation function. Electrons in lower shells were treated within the frozen core approximation.[13a] A set of auxiliary s, p, d, f, and g functions,[17] centred in all nuclei, was introduced in order to fit the molecular density and Coulomb potential accurately in each SCF cycle. Both geometry optimisations and energy evaluations have been fully carried out within a generalised gradient approximation (GGA) that includes a GGA exchange and correlation corrections of Becke[18] and Perdew (BP86).[19]

In order to validate the method, the XRD data of complex **2** was geometrically optimised by excluding the solvent molecules. The results show good agreement between the experimental and theoretical data. The experimental and theoretical bond lengths and angles differ by less than 0.08 Å and 3.6°, respectively. The standard deviations for the selected distances and angles listed in Figure 3 were 0.04 Å and 2.1°, respectively, which confirm the validity of the chosen computational method.

All the experimental compounds were analysed computationally. It was found experimentally that both mononuclear and binuclear species are diamagnetic. For this reason, optimisations were carried out for neutral closed-shell singlet ground-state structures. However, since it has been found that the triplet state is close in energy to the singlet state, or it can be even more stable than the singlet state, we checked the relative stability of both states for all compounds by optimising the triplet state. In all cases the triplet state geometry presented a higher energy, indicating that the singlet states are the most favourable. This is in agreement with the sharp peaks in the NMR spectra. The difference between these two states is around 20 kcal·mol^{-1} (racemic-trans-**1** 22.2 kcal·mol^{-1}; meso-trans-**1** 21.4 kcal·mol^{-1}; racemic-trans-**2** 19.4 kcal·mol^{-1}; meso-trans-**2** 21.6 kcal·mol^{-1}).

Energy calculations predicted a slight stabilisation, by less than 0.1 kcal·mol^{-1}, of the meso-trans-**1** isomer relative to the racemic-trans-**1**, showing that the two isomers have similar energies, in line with the fact that experimentally the two isomers are present as final products. On the other hand, the energy calculations on complex **2** gave an energy difference of 5.1 kcal·mol^{-1} between the racemic-trans-**2** and the meso-trans-**2** isomers, in agreement with an equilibrium strongly displaced towards the racemic-trans-**2** diastereomer (experimental $\Delta E \geq 2.3$ kcal·mol^{-1}).[11]

We also attempted to optimise an anti conformation for the binuclear complex, but the optimisation process evolved towards the racemic-trans-**2** species, as the anti conformations are even less stable than the syn ones because of the steric requirements of the ligands.

Conclusion

In conclusion, the calculated energy differences between the racemic-trans and meso-trans diastereomers of these phosphanylthiolato complexes of Ni^{II} are in agreement with the experimentally observed racemic-trans/meso-trans ratios and are responsible for the chiral recognition between the two enantiomeric forms of the racemic ligand. This phenomenon is especially important in the binuclear complex **2**, in which a destabilised anti conformation of the bridging sulfurs would be necessary in order for the meso-trans isomer to be stable.

Experimental Section

General Remarks: The complexes were synthesised using standard Schlenk techniques under nitrogen atmosphere. The solvents were dried by standard methods and distilled and deoxygenated before use. The C, H and S analyses were carried out using a Carlo–Erba microanalyser. CDCl$_3$ for NMR measurements was dried over molecular sieves. Proton NMR spectra were recorded at 200 MHz on a Bruker DPX-200 spectrometer. Peak positions are relative to tetramethylsilane as internal reference. ^{31}P{^{1}H} NMR spectra were recorded on the same instrument operating at 81.0 MHz. Chemical shifts are relative to external 85 % H$_3$PO$_4$ and downfield values are reported as positive. ^{13}C{^{1}H} NMR spectra were recorded on the same instrument operating at 50.3 MHz. Chemical shifts are relative to tetramethylsilane as internal reference.

[Ni{SCH(CH$_3$)CH$_2$PPh$_2$-*P,S*}$_2$] (1): 1-(diphenylphosphanyl)propane-2-thiol (205.4 mg, 0.79 mmol) in CH$_2$Cl$_2$ (1 mL) was added to a solution of NiCl$_2$·6H$_2$O (75.1 mg, 0.316 mmol) in methanol (2 mL) under a nitrogen atmosphere to produce a green precipitate. The precipitate was washed with hexane yielding complex **1** (155.1 mg, 80 %). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ = 1.31 (d, ^3J = 6.4 Hz, 2.72 H, CH$_3$ racemic-trans-**1**); 1.40 (d, ^3J = 6.2 Hz, 6 H, CH$_3$ meso-trans-**1**); 2.33 (tt, ^2J = −13.4, ^3J = 13.4, $^2J_{H,P}$ ≈ 2.8 Hz, 2 H, CH$_{2ax.}$ meso-trans-**1**); 2.47 (ddt, ^2J = −13.1, ^3J = 10.1, $^2J_{H,P}$ ≈ 3.0 Hz, 0.92 H, CH$_{2ax.}$ racemic-trans-**1**); 2.6−3.0 (m, 5.8 H, CH$_2$ equiv., CH, meso-trans-**1** and racemic-trans-**1**); 7.1−8.3 (m, 29 H, H$_{ar}$) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, TMS): δ = 25.10 (t, $J_{C,P}$ = 9.0 Hz, CH$_3$ meso-trans-**1**); 26.08 (t, $J_{C,P}$ = 7.4 Hz, CH$_3$ racemic-trans-**1**); 36.37 (t, $J_{C,P}$ = 12.3 Hz, CH meso-trans-**1**); 37.22 (t, $J_{C,P}$ = 14.4 Hz, CH racemic-trans-**1**); 46.51 (t, $J_{C,P}$ = 18.5 Hz, CH$_2$ meso-trans-**1**); 47.44 (t, $J_{C,P}$ = 18.2 Hz, CH$_2$ racemic-trans-**1**); 128.5−129.2 (m, C$_m$ meso-trans-**1** and racemic-trans-**1**); 129.2−132.3 (m, C$_i$ meso-trans-**1** and racemic-trans-**1**); 130.66 (s, C$_p$ meso-trans-**1**); 130.79 (s, C$_p$ racemic-trans-**1**); 131.23 (s, C′$_p$ racemic-trans-**1**); 131.41 (s, C′$_p$ meso-trans-**1**); 132.85 (t, $J_{C,P}$ = 5.4 Hz, C$_o$ meso-trans-**1**); 133.41 (t, $J_{C,P}$ = 5.6 Hz, C$_o$ racemic-trans-**1**); 134.58 (t, $J_{C,P}$ = 6.1 Hz, C′$_o$ racemic-trans-**1**); 135.10 (t, $J_{C,P}$ = 6.1 Hz, C′$_o$ meso-trans-**1**) ppm. ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, H$_3$PO$_4$): δ = 52.56 (s, 1P, meso-trans-**1**); 54.23 (s, 0.46P, racemic-trans-**1**) ppm. C$_{30}$H$_{32}$NiP$_2$S$_2$ (577.4): calcd. C 62.41, H 5.59, S 11.11; found C 62.22, H 5.70, S 10.99 %.

[Ni{μ-SCH(CH$_3$)CH$_2$PPh$_2$-*P,S*}(Cl)]$_2$ (2): 1-(diphenylphosphanyl)propane-2-thiol (88.1 mg, 0.338 mmol) in CH$_2$Cl$_2$ (1 mL) was added to a solution of NiCl$_2$·6H$_2$O (80.5 mg, 0.338 mmol) in methanol (2 mL) under a nitrogen atmosphere. The green precipitate obtained had redissolved after 3 h stirring, yielding a brown solution. The product was crystallised by addition of diethyl ether to afford complex **2** as brown crystals (91.3 mg, 80 %). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ = 1.34 (d, ^3J = 8.0 Hz, 6 H, CH$_3$); 2.34 (td, ^2J = −13.7, ^3J = 13.7, $^2J_{H,P}$ = 6.4 Hz, 2 H, CH$_{2ax.}$); 2.63

(ddpseudo-t, $^2J = -13.7$, $^3J = 4.5$, $^2J_{H,P} \approx 4.4$ Hz, 2 H, CH$_2$ equiv.); 3.24 (m, 2 H, CH); 7.2−8.4 (m, 20 H, H$_{ar}$) ppm. ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, TMS): δ = 22.96 (m, CH$_3$); 39.16 (pseudo-t, $J \approx 3.0$ Hz, CH); 44.97 (d, $^1J_{C,P} = 38.8$ Hz, CH$_2$); 128.80 (pseudo-t, $^3J_{C,P} = 5.2$ Hz, C$_m$); 128.95 (pseudot, $^3J_{C,P} = 5.2$ Hz, C$'_m$); 130.12 (dd, $^1J_{C,P} = 6.7$, $^4J_{C,P} \approx 3.1$ Hz, C$_i$); 131.09 (dd, $^1J_{C,P} = 5.6$, $^4J_{C,P} \approx 3.0$ Hz, C$'_i$); 131.84 (s, C$_p$); 133.14 (pseudo-t, $J_{C,P} \approx 4.9$ Hz, C$_o$); 133.63 (pseudo-t, $J_{C,P} \approx 5.1$ Hz, C$_o$) ppm. ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$, H$_3$PO$_4$): δ = 36.28 (s) ppm. C$_{30}$H$_{32}$Cl$_2$Ni$_2$P$_2$S$_2$ (707.0): calcd. C 50.97, H 4.56, S 9.07; found C 50.66, H 4.69, S 8.93 %.

X-ray Structure Determination of 2: Brown crystals of **2** were obtained by slow evaporation of a chloroform/dichloromethane (1:1) solution at room temperature. Molecular formula: C$_{31}$H$_{33}$Cl$_5$Ni$_2$P$_2$S$_2$; $M = 826.30$; monoclinic; $a = 12.8894(4)$, $b = 11.8883(3)$, $c = 22.5265(7)$ Å, β = 96.5500(10)°, $V = 3429.27(17)$ Å^3; space group $P2_1/n$; $Z = 4$, μ = 1.725 mm^{-1}, $D_{calcd.} = 1.600$ g cm^{-3}. The measurements were made on a Siemens P4 diffractometer equipped with a SMART-CCD-1000 area detector, a MAC Science Co. rotating anode with Mo-$K_α$ radiation, a graphite monochromator and a Siemens low temperature device LT2 ($T = -120$ °C). In the range 1.74 to 31.50°, 49317 reflections were collected, of which 10947 were unique ($R_{int} = 0.0838$). Full-sphere data was collected using ω and scans. Programs used: Data collection Smart V. 5.060 (Bruker AXS, 1999), data reduction Saint + Version 6.02 (Bruker AXS 1999) and absorption correction SADABS (max/min transmission: 1.000000/0.356109, Bruker AXS 1999). Structure solution and refinement was done using SHELXTL Version 5.10 (Sheldrick, Universtität Göttingen, Göttingen (Germany), 1998). The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2. All hydrogen atoms were refined without constraints. Final $R_1[I > 2σ(I)] = 0.0452$ and $wR(F^2)[I > 2σ(I)] = 0.1037$. The number of refined parameters was 511. CCDC-216078 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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