73. Preparation and Properties of Bis[μ-*S*-(2-thiolatoethyl)-diphenylphosphine][(2-thiolatoethyl)diphenyl-phosphine]dinickel(+1) Ion, a Novel Unsymmetrical Thiolate-bridged Complex

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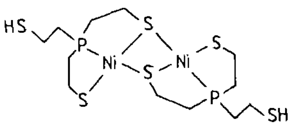
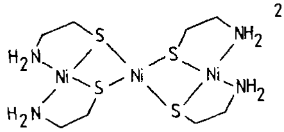
Summary

The title cation (= $Ni_2L_3^+$) is formed in a variety of reactions (*Schemes 1* and *2*) in systems containing Ni^{2+} and (2-thiolatoethyl)-diphenylphosphine (= L^-) in the absence of coordinating anions at Ni^{2+}/L^- ratios > 0.5 in apolar or moderately polar media. Solid $[Ni_2L_3]ClO_4$ and $[Ni_2L_3]BPh_4$ have been isolated. *Job*'s plots confirm the $Ni_2L_3^+$-stoichiometry in solution. ^{31}P-NMR data are consistent with $\geqslant 97\%$ $Ni_2L_3^+$ (*vs.* $\leqslant 3\%$ of hypothetical $Ni_3L_4^{2+}$) at equilibrium and support the suggested configuration (*Fig. 2*). The equilibrium between $NiL_2 + NiL_2Br_2$ and $Ni_2L_3^+ + Br^-$ varies with the solvent composition in CH_2Cl_2/EtOH mixtures. The rate of formation of $Ni_2L_2Br_2$ from $Ni_2L_3^+$ and bromide (in high excess) in CH_2Cl_2 is first-order in $[Ni_2L_3^+]_{tot}$ but depends on the ratio $[Bu_4NBr]_{tot}/[Ni_2L_3 \cdot ClO_4]_{tot}$, even at a high excess of bromide. This is interpreted by efficient competition in ion-aggregate formation between the small perchlorate concentration introduced as the counterion of $Ni_2L_3^+$, and the large excess of bromide.

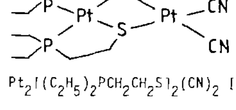
Introduction. – Thiolate donors coordinated to one metal ion are characterized by their strong residual nucleophilicity which enables them to act as bridging ligands to a second metal centre. Owing to the important role of polynuclear metal thiolato complex structures in biological systems, their chemistry has been developed rapidly in the last few years and has been reviewed recently [1]. More specifically, polynuclear com-



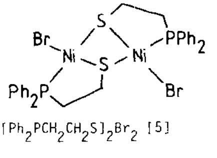
$Ni_2[P(CH_2CH_2S)_2CH_2CH_2SH]_2$ [2]



$Ni_3(H_2NCH_2CH_2S)_4^{2+}$ [3]



$Pt_2[(C_2H_5)_2PCH_2CH_2S]_2(CN)_2$ [4]



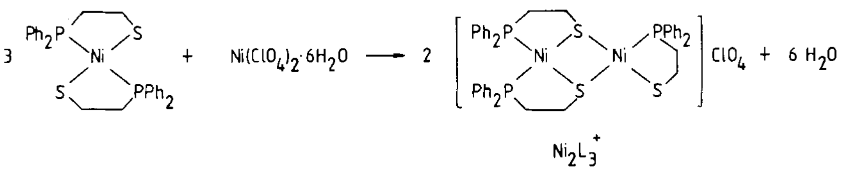
$Ni_2[Ph_2PCH_2CH_2S]_2Br_2$ [5]

plexes of chelating ligands with at least one thiolate donor group have been known for some time, particularly with metal centres of square planar coordination. Some known structures are represented above.

A common feature of these structures (which all have two thiolate bridges between the metal centres) is their idealized C_2- or C_s-symmetry. In this communication, we report on our unexpected finding of an *unsymmetrical* (C_1) binuclear nickel complex with the ligand (2-thiolatoethyl)diphenylphosphine (= L^-). This species is formed in different reactions under a variety of conditions. Some of its reactions to form other, known complexes of the same ligand are described.

Results. – The reaction of green bis[(2-thiolatoethyl)diphenylphosphine]nickel(II), NiL_2, with one-third equivalent of hydrated nickel perchlorate in CH_2Cl_2/acetone 1:1 produces a brown solution from which $[Ni_2L_3]ClO_4$ can be crystallized. Its VIS spectrum is distinctly different from that of NiL_2, and the observed increase in molar absorptivity in the whole UV/VIS region is characteristic of thiolate bridge formation. The elemental analysis allows clear distinction from similar compositions such as $[Ni_3L_4](ClO_4)_2$. The $Ni_2L_3^+$-stoichiometry in solution is inferred from a determination by *Job*'s method of continuous variation [6] of the Ni^{2+}/NiL_2 ratio in CH_2Cl_2/acetone 4:1 at $\lambda = 375$ nm. The two components react in the suggested 1:3 ratio according to *Scheme 1*[1]). The *Job* plot *(Fig. 1)* suggests a high formation constant ($K > 10^4$) by this route and there is no evidence for further polynuclear species under the experimental conditions.

Scheme 1



The ^{31}P-NMR spectrum of $Ni_2L_3^+$ is virtually independent of the nature of the non-coordinating counter-anion (ClO_4^-, BPh_4^-) and represents a case of a deceptively simple *ABX*-spectrum. *Figure 2* shows the measured and simulated spectra of $[Ni_2L_3]ClO_4$ at 36.43 MHz in $CDCl_3$, as well as the proposed structure.

The cation $Ni_2L_3^+$ is also formed by reaction of an equimolar mixture of NiL_2 and $[NiL(Ph_2PCH_2CH_2SBzl)]BPh_4$ in $CHCl_3$ or in CH_2Cl_2 *(Scheme 2)*. The ^{31}P-NMR spectrum of this mixture was run in CH_2Cl_2 and in PhCl. In CH_2Cl_2, the reaction mixture contains $[Ni_2L_3]BPh_4$ and the presumed *P*-alkylation product $[PhP(CH_2Cl)$-$CH_2CH_2SBzl]Cl$. In the non-alkylating solvent PhCl, $[Ni_2L_3]BPh_4$ precipitated and was

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[1]) The kinetics of this reaction have been explored by repetitive VIS spectral scans. The transformation is at least biphasic and the most rapid phase is completed to 90% or more in $\leqslant 5$ min. The whole reaction sequence is finished in *ca.* 24 h. In these experiments, an isosbestic point at $\lambda = 375$ nm between the species present after the most rapid phase and the final products was found. Accordingly, optical densities for *Job*'s plots were recorded after 20 h at this wavelength, thus eliminating interference from intermediate reaction phases or possible slower side reactions.

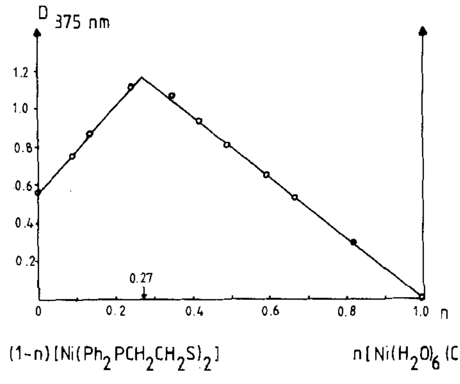
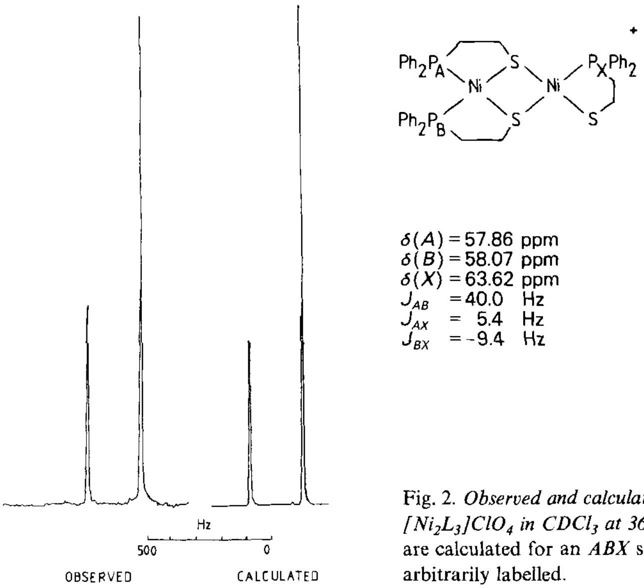


Fig. 1. Job's *curve of the system* $NiL_2/Ni(H_2O)_6(ClO_4)_2$ *in* CH_2Cl_2*/acetone 4:1.* n is the mole fraction, $[Ni^{2+}]_{tot} = 3.93 \times 10^{-4}$ M, l = 1 cm.



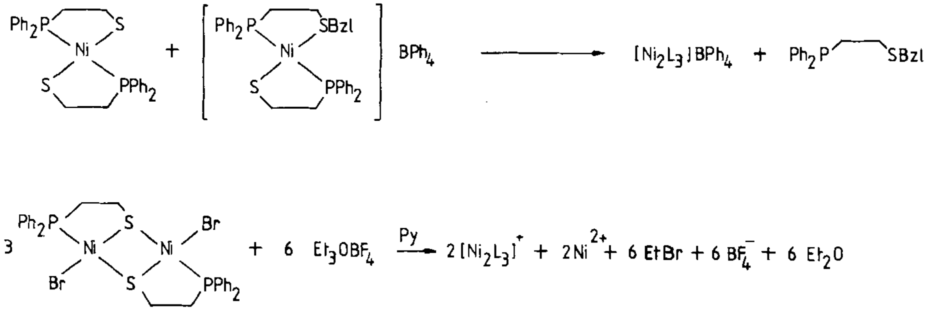
$\delta(A) = 57.86$ ppm
$\delta(B) = 58.07$ ppm
$\delta(X) = 63.62$ ppm
$J_{AB} = 40.0$ Hz
$J_{AX} = 5.4$ Hz
$J_{BX} = -9.4$ Hz

Fig. 2. *Observed and calculated* ^{31}P*-NMR spectra of* $[Ni_2L_3]ClO_4$ *in* $CDCl_3$ *at 36.43 MHz.* The indicated values are calculated for an *ABX* spin system. *A* and *B* are arbitrarily labelled.

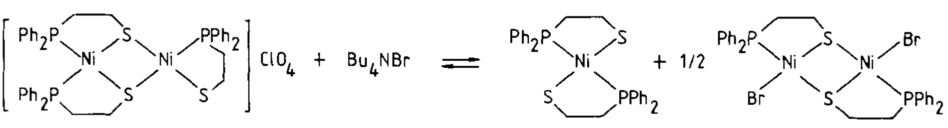
identified after isolation by its VIS spectrum. In the mother liquor were detected $Ph_2PCH_2CH_2SBzl$ as well as traces of $Ni_2L_3^+$ and of the starting materials.

Similarly, alkylation of $Ni_2L_2Br_2$ in CH_2Cl_2 with Et_3OBF_4 *(Scheme 2)* in the presence of pyridine also leads to nearly quantitative formation of $Ni_2L_3^+$. The reaction was followed by VIS spectrophotometry and the concentration of $Ni_2L_3^+$ in the final spectrum corresponds to ⅔ of the initial concentration of $Ni_2L_2Br_2$, confirming the stoichiometry proposed in *Scheme 2*. Furthermore, $Ni_2L_3^+$ is the only species detected by ^{31}P-NMR spectroscopy in the reaction mixture.

Scheme 2



Scheme 3



In aprotic solvents such as PhCl, CH_2Cl_2 or acetone, $[Ni_2L_3]ClO_4$ reacts with Bu_4NBr according to *Scheme 3*. In these solvents, a mixture of NiL_2 and $Ni_2L_2Br_2$ [5] [7] [8] in the ratio 2:1 is formed to $\geqslant 90\%$. Another, minor product ($\leqslant 10\%$) is detected by ^{31}P-NMR in $CDCl_3$ and in PhCl (see *below*). On the other hand, this equilibrium lies

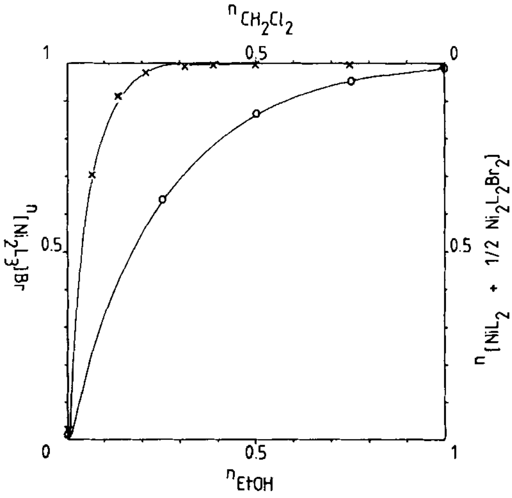
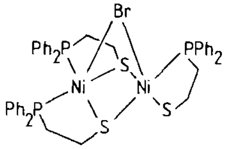


Fig. 3. *Product composition in mole fractions n of the system 2 NiL_2 + $Ni_2L_2Br_2$ $\rightleftharpoons$ 2 $[Ni_2L_3]Br$ in function of the mole fraction $n_{CH_2Cl_2}$ or n_{EtOH} of CH_2Cl_2/EtOH mixtures.* (×): $[Ni]_{tot} = 0.366 \times 10^{-3}$ M, at 372 nm; (○): $[Ni]_{tot} = 1.998 \times 10^{-3}$ M, at 520 nm.

far to the left in protic solvents (MeOH, EtOH) as shown by spectrophotometric measurements at 375 and 520 m.

Fig. 3 shows the distribution of the major products, $Ni_2L_3^+$, NiL_2 and $Ni_2L_2Br_2$, of the reaction in *Scheme 3* in function of the mole fraction of CH_2Cl_2/EtOH mixtures used. Two curves were measured for different total complex concentration. Measurements at still higher concentrations were limited by the insolubility of NiL_2 in mixtures rich in EtOH.

The ^{31}P-NMR spectrum of an equilibrium mixture of $[Ni_2L_3]ClO_4$ and Bu_4NBr (1:1) in (D_5)PhCl shows as the main components the species NiL_2 and $Ni_2L_2Br_2$ as well as an *ABX*-pattern for a minor component (< 10%) with $\delta_A = 56.5$, $\delta_B = 58.6$, $\delta_X = 62.7$ ppm; $|^2J_{AB}| = 40$, $|^4J_{AX}| = 2.25$, $|^4J_{BX}| = 6.05$ Hz. In another experiment, a solution of $[Ni_2L_3]ClO_4$ in $CDCl_3$ was cooled to −35°C and showed after addition of one equivalent of Bu_4NBr the above *ABX*-pattern as the only feature. The sample was then kept at room temperature for 10 min and measured again at −35°C to show the additional signals of NiL_2 and $Ni_2L_2Br_2$. Apparently, the reaction between $Ni_2L_3^+$ and Br^- to give the species producing the *ABX*-pattern is much more rapid than the transformation into NiL_2 and $Ni_2L_2Br_2$. This species, presumably $[Ni_2L_3 \cdot Br]$, is a likely intermediate in the reaction in *Scheme 3*. The presence of bromide causes a characteristic change of the spectrum of $Ni_2L_3^+$ *(Fig. 2)* in that the difference between δ_A and δ_B becomes much greater. The effect is essentially independent of solvent ((D_6)acetone, $CDCl_3$, (D_5)PhCl), temperature (−35°C, +25°C) and spectrometer frequency (36.43–81.03 MHz). This change is consistent with strong association of bromide, either by formation of contact ion pairs in the media of low dielectric constant or by coordination of bromide as a third, bridging ligand between the two nickel centres²).



The kinetics of the reaction of $[Ni_2L_3]ClO_4$ with Bu_4NBr in CH_2Cl_2 were examined cursorily under pseudo-first-order conditions using $[Ni_2L_3]ClO_4$ as the limiting reagent. Spectrophotometric runs at 372 nm gave linear plots of log $|D-D_\infty|$ *vs.* t for 4–5 half lives. The rate is therefore first-order in the starting complex. However, the observed rate constants varied with the initial concentration of $[Ni_2L_3]ClO_4$, and this indicates that the perchlorate anion introduced with the complex influences the rate. We interpret this as the effect of competitive ion pairing of $Ni_2L_3^+$ with either Br^- or ClO_4^-. The *Table* shows that the influence of the ion-pairing with ClO_4^- (present at much smaller concentrations than Br^-) extends to high ratios of $[Bu_4NBr]_{tot}/[Ni_2L_3 \cdot ClO_4]_{tot}$; for the ratio ≈ 1200, the rate reaches a maximum and then decreases again. This complex-ion association phenomenon precludes determination of the reaction order in $[Br^-]$, since

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²) Good evidence for this mode of coordination has been found in the compound $\{Ni_2[(\pm)\text{-}CH_3SCH_2CH_2P(Ph)CH_2CH_2CH_2P(Ph)CH_2CH_2S]_2 \cdot I\}ClO_4$ [9], with similar effects on the ^{31}P-NMR spectra.

Table. *Pseudo-first-order Rate Constants for the Reaction* $[Ni_2L_3]ClO_4 + Bu_4NBr \rightleftharpoons NiL_2 + \frac{1}{2}\ Ni_2L_2Br_2$ *in* CH_2Cl_2 *at 25°*

$[Ni_2L_3 \cdot ClO_4]$ $[(\text{mole dm}^{-3}) \times 10^5]$	$[Bu_4NBr]$ $[(\text{mole dm}^{-3}) \times 10^2]$	$[Br^-]_{tot}/[ClO_4^-]_{tot}$	k_{obs} $[s^{-1}]$
10.26	4.81	469	5.04
4.10	4.81	1173	7.20
1.64	4.81	2933	6.81
0.66	4.81	7320	6.04
13.0	0.93	72	3.71
5.71	0.91	159	6.43

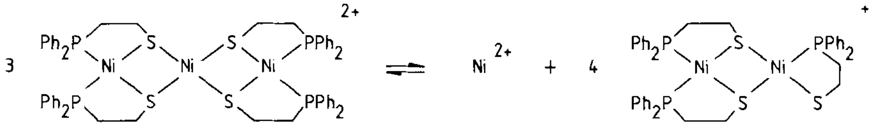
any appreciable variation of the bromide concentration will also alter the critical $[Bu_4NBr]_{tot}/[Ni_2L_3 \cdot ClO_4]_{tot}$ ratio.

Discussion. – The formation of the cation $Ni_2L_3^+$ is, to our knowledge, unprecedented and surprising in view of the ample evidence for formation of similar, symmetric cations $Ni_3L'^{2+}_4$ with a variety of bidentate ligands (*e.g.* L' = diethyl(2-thiolatoethyl)phosphine [5], butyl(2-thiolatoethyl)phenylphosphine [8], (2-thiolatoethyl)amines [10] [11], 2-(2-thiolatoethyl)pyridine [12]). On the other hand, the ligands L' (*tert*-butyl)(2-thiolatoethyl)amine and diethyl(2-thiolatoethyl)amine have been reported to fail to give $Ni_3L'^{2+}_4$-species. This has been attributed to the steric effect of the bulky substituents on the nitrogen donor atoms [11].

Apart from direct reaction of NiL_2 with Ni^{2+}, cation $Ni_2L_3^+$ is formed from mixed ligand species by displacement of ligands ≠L or by bromide abstraction with Et_3OBF_4 (*Scheme 2*). The latter reaction resembles known alkylative halide abstraction [13], but the presence of pyridine is essential here.

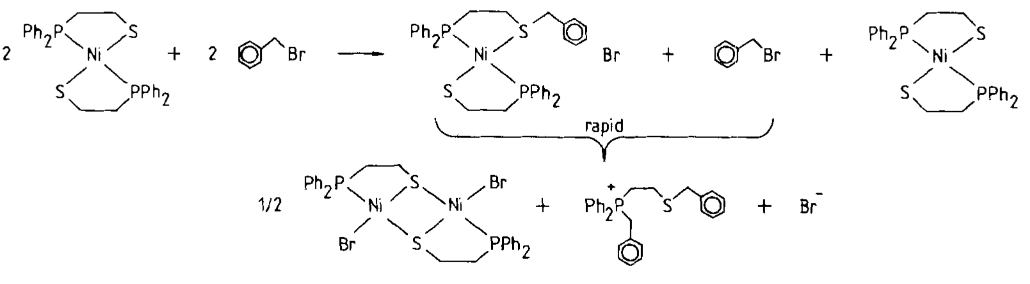
Both in $Ni_2L_3^+$ and in (hypothetical) $Ni_3L_4^+$, the polynuclear systems are destabilized by the steric demands of two diphenylphosphino substituents in *cis*-position on a nickel center. We make the following assumptions: *1*) steric destabilization is essential for the position of the hypothetical equilibrium in *Scheme 4*. *2*) The steric destabilization energy is the same for every *cis*-$(R_2PCH_2CH_2S^-)_2$Ni-moiety in polynuclear species. This steric destabilization energy increment arises six times on the left-hand side and four times on the right-hand side of the equation in *Scheme 4*. Formation of $Ni_2L_3^+$ is thus preferred if the reduction of steric destabilization outweighs the free energy of release of Ni^{2+} from the polynuclear species. The formation of $Ni_2L_3^+$ from $NiL_2 + Ni^{2+}$ (or from hypothetical $Ni_3L_4^{2+}$) represents a reduction of the ionic strength and is particularly favored in solvents of low dielectric constant.

Scheme 4



The equilibrium involving bromide *(Scheme 3)* is also influenced by the solvent polarity. As the mole fraction of the specific anion solvator, EtOH [14] decreases, there is more extensive coordination of bromide to form a non-electrolyte. Indeed, the kinetics of this reaction in CH_2Cl_2 reveals a high degree of ion association. Under these circumstances, it may appear surprising that no deviation from pseudo-first-order kinetics was observed since the perchlorate activity is anticipated to change appreciably in the course of each individual run. The observed result can be taken to indicate essentially equal strength of association of ClO_4^- with $Ni_2L_3^+$ and Bu_4N^+. In this case, kinetics of first-order in $[Ni_2L_3]_{tot}$ are possible at sufficiently high $[Br^-]_{tot}/[ClO_4^-]_{tot}$ ratios, such as to maintain $[Bu_4NBr]$ essentially constant.

Scheme 5



The present work provides a clue to some unexpected features in the *S*-, *P*-alkylation reaction [6] of NiL_2 *(Scheme 5)*. When NiL_2 is reacted with a stoichiometrically deficient quantity of benzyl bromide, *e.g.* 1 equivalent, the monoalkylated intermediate, $[NiL(Ph_2PCH_2CH_2SBzl)]^+$, is not detected. This is because it reacts with Br^- to form $Ni_2L_2Br_2$ and $Ph_2PCH_2CH_2SBzl$ which, in turn, will be alkylated by the remaining benzyl bromide to give $Ph_2P(Bzl)CH_2CH_2SBzl^+$, leaving the corresponding amount ($\lesssim 50\%$) of unreacted NiL_2. In more polar solvents, $Ni_2L_3^+$ will be formed as shown above. These transformations are sufficiently rapid to compete with the *S*-alkylation of the second ligand; their consequences to the general pattern of alkylation reactions at coordinated thiolate will be discussed in a subsequent communication.

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Experimental Part

General. Reagent grade solvents were distilled from P_2O_5 (CH_2Cl_2) or BaO (C_2H_5OH) or molecular sieves; other reagents were used as purchased. UV/VIS absorption spectra and kinetics were measured on a *Pye Unicam 1800* spectrophotometer at 25 ± 0.1° maintained by a *Haake B/N3* thermostat. ^{31}P-NMR spectra were recorded on *Bruker HX 90-E, CPX-200, WP-200,* or *Varian XL-100* instruments in the FT mode, relative to ext.

85% H_3PO_4 standard. Elemental analyses were performed by the Mikrolabor, ETH Zürich (C,H,N), or by the Analytisches Labor des Laboratoriums für Anorganische Chemie, ETH-Zürich. (2-Mercaptoethyl)diphenylphosphine was prepared by known procedures [8] [16].

trans-*Bis[(2-thiolatoethyl)diphenylphosphine]nickel(II)* (NiL_2). To a solution of (2-mercaptoethyl)-diphenylphosphine (24.1 g, 98 mmol) in deoxygenated CH_3CN (100 ml) was added dropwise under a N_2 atmosphere a deoxygenated solution of hexaquanickel(II) dinitrate (13.96 g, 48 mmol) in MeOH (80 ml). A green powder precipitated and was recrystallized from DMF to yield 24.15 g (91%) of crystalline platelets. UV/VIS (CH_2Cl_2, 25°): max. 593 (97), 370 (1370); min. 519 (33), 361 (1330). ^{31}P-NMR (80.99 MHz, $CDCl_3$): 66.5 (*s*); 36.43 MHz, C_6D_5Cl): 65.6 (*s*). Anal. calc. for $C_{28}H_{28}NiP_2S_2$ (549.32): C 61.22, H 5.14, P 11.28, S 11.68, Ni 10.69; found: C 60.97, H 5.23, P 11.22, S 11.64, Ni 10.87.

Tris[(2-thiolatoethyl)diphenylphosphine]dinickel(II) Perchlorate ($[Ni_2L_3]ClO_4$). To a solution of *trans*-bis[(2-thiolatoethyl)diphenylphosphine]nickel(II) (411 mg, 0.75 mmol) in CH_2Cl_2 (25 ml) was added dropwise a solution of hexaquanickel(II) diperchlorate (91 mg, 0.25 mmol) in acetone (25 ml). The color of the solution changed from green to brown and the reaction mixture was heated to reflux for 1 h. The solvent was then evaporated *in vacuo* and the residue was recrystallized from acetone/Et_2O to yield 395 mg (83%) of the product. UV/VIS (CH_2Cl_2, 25°): max. 660 (230); min. 621 (200); sh 530 (700), ≈ 420 (3000), ≈ 380 (6150). ^{31}P-NMR (36.43 MHz, $CDCl_3$): 63.6 (*2 lines*, 1P); 58.0 (*2 lines*, 2P). $\Lambda_e(10^{-3}$ mol dm^{-3}, CH_3NO_2, 25°$) = 78\ \Omega^{-1}$ cm^2 mol^{-1}. Anal. calc. for $C_{42}H_{42}ClNi_2O_4P_3S_3$ (952.71): C 52.95, H 4.45, Cl 3.72; found: C 52.73, H 4.60, Cl 3.45.

Tris[(2-thiolatoethyl)diphenylphosphine]dinickel(II) Tetraphenylborate ($[Ni_2L_3]BPh_4$). To a solution of tris[(2-thiolatoethyl)diphenylphosphine]dinickel(II) perchlorate (930 mg, 0.98 mmol) in acetone (100 ml) was added dropwise under reflux a solution of $NaBPh_4$ (3 g, 8.8 mmol) in EtOH (30 ml). The red-brown product started to precipitate and the reaction mixture was stirred for 0.5 h under reflux, and then allowed to cool. The filtered product was washed with EtOH and dried *in vacuo*. Yield: 1.11 g (0.95 mmol, 97%). ^{31}P-NMR (80.99 MHz, $CDCl_3$): 64.3 (*m*, 1P); 58.3 (*m*, 2P). Anal. calc. for $C_{66}H_{62}BNi_2P_3S_3$ (1172.57): C 67.61, H 5.33; found: C 67.58, H 5.43.

trans-*Dibromobis[(2-thiolatoethyl)diphenylphosphine]dinickel(II)* ($Ni_2L_2Br_2$). In a sealed tube 300 mg (0.55 mmol) of bis[(2-thiolatoethyl)diphenylphosphine]nickel(II) and 406 mg (0.55 mmol) of dibromobis(triphenylphosphine)nickel(II) in 20 ml of abs. PhCl were heated for 24 h at 70°. The resulting red solution was evaporated to dryness. The residue was recovered as black-red crystals from hot abs. acetone, and recrystallized from acetone/benzene to yield 235 mg (56%) of the product. UV/VIS (CH_2Cl_2, 25°): max. 503 (2980), 400 (3670); min. 443 (2280), 370 (2490). ^{31}P-NMR (80.99 MHz, $CDCl_3$): 53.7 (*s*); (36.43 MHz, C_6D_5Cl): 52.5 (*s*). Anal. calc. for $C_{28}H_{28}Br_2Ni_2P_2S_2$ (767.78): C 43.80, H 3.68, Ni 15.29, Br 20.81; found: C 43.82, H 3.70, Ni 15.18 ± 0.30, Br 20.40 ± 0.40.

2-(Benzylthio)ethyldiphenylphosphine. (2-Mercaptoethyl)diphenylphosphine (12.1 g, 49.2 mmol) was dissolved in anh., degassed EtOH. Small Na chips (1.13 g, 49.1 mmol) were dissolved in this solution to which benzyl bromide (8.2 g, 47.9 mmol) was added within 30 min. NaBr precipitated and the suspension was heated under reflux for 2 h. The solvent was removed under reduced pressure and the residue was dissolved in $CHCl_3$ (40 ml) and extracted with deoxygenated H_2O (3 × 40 ml). After evaporating the $CHCl_3$, the resulting clear, colorless oil was distilled *in vacuo*. A first, small fraction (91–147°/0.25 Pa) was followed by the desired product (10.1 g 64%, 147–156°/0.25 Pa, bath temperature 220°). A further quantity could not be distilled, but was recovered as the nickel complex. ^{1}H-NMR (60 MHz, $CDCl_3$, int. TMS): 7.5–7.3 (*m*, 15H); 3.8 (*s*, 2H); 2.3–2.8 (*m*, 4H). ^{31}P-NMR (36.43 MHz, CH_2Cl_2/ext. (D_6)acetone): −17.2 (*s*). Anal. calc. for $C_{21}H_{21}PS$ (336.41): C 74.97, H 6.29; found: C 74.59, H 6.54.

Bis[(2-benzylthio)ethyldiphenylphosphine]nickel(II) Diperchlorate. To a solution of (2-benzylthio)ethyl-diphenylphosphine (1.35 g, 4 mmol) in 4 ml of oxygen-free acetone was added dropwise under an inert atmosphere a solution of hexaquanickel(II) diperchlorate (0.77 g, 2.1 mmol) in oxygen-free acetone (10 ml). To the resulting yellow-red solution were added 15 ml of oxygen-free Et_2O to precipitate the yellow product which was washed with Et_2O and dried *in vacuo*. Yield: 1.51 g (81%). Anal. calc. for $C_{42}H_{42}Cl_2NiO_8P_2S_2$ (930.43): C 54.21, H 4.55; found: C 53.80, H 4.47.

[(2-Thiolathoethyl)diphenylphosphine][(2-benzylthio)ethyldiphenylphosphine]nickel(II) Tetraphenylborate. An oxygen-free solution of bis[(2-benzylthio)ethyldiphenylphosphine]nickel(II) diperchlorate (60.5 mg, 0.065 mmol) and *trans*-bis[(2-thiolatoethyl)diphenylphosphine]nickel(II) (35.7 mg, 0.065 mmol) in acetone (7 ml) was refluxed for 2 h, filtered and the volume reduced to 3 ml. To this red-brown solution was added dropwise a solution of $NaBPh_4$ (342 mg, 1 mmol) in EtOH (20 ml) to precipitate a red crystalline product which was filtered, washed with EtOH and dried *in vacuo*. Yield: 100 mg (80%). The ^{31}P-NMR spectrum (80.99 MHz, $CDCl_3$) of the analytically pure product shows a first *AB*-pattern ($\delta_A = 68.7$, $\delta_B = 58.8$; $|^2J_{AB}| = 260$) attributed

to the *trans*-isomer on the base of the coupling constant and a second *AB*-pattern ($\approx 5\%$ of total intensity) attributed to the *cis*-isomer ($\delta_A = 69.2$, $\delta_B = 52.0$; $|^2J_{AB}| = 44$) in equilibrium. Anal. calc. for $C_{59}H_{55}BNiP_2S_2$ (959.61): C 73.85, H 5.78; found: C 73.68, H 5.75.

Reaction of NiL_2 with [(2-Thiolatoethyl)diphenylphosphine][(2-benzylthio)ethyldiphenylphosphine]nickel(II) Tetraphenylborate. A suspension of 3.3 mg (6×10^{-6} mol) NiL_2 and 5.76 mg (6×10^{-6} mol) [(2-thiolatoethyl)diphenylphosphine][(2-benzylthio)ethyldiphenylphosphine]nickel(II) tetraphenylborate in PhCl was stirred under a N_2 atmosphere for 2 weeks. The brown solid was filtered and analysed for $[Ni_2L_3]BPh_4$ by VIS spectrophotometry: 6.8 mg (5.8×10^{-6} mol, 97%). ^{31}P-NMR (81.03 MHz, PhCl/(D_6)DMSO) of the mother liquor: -16.78 ($Ph_2PCH_2CH_2SBzl$); 66.2 (traces of NiL_2); 68.7, 57.9, $J_{AB} = 260$ Hz (traces of [(2-thiolatoethyl)diphenylphosphine]([2-benzylthio)ethyldiphenylphosphine]nickel(II) tetraphenylborate); 64.0, 57.7 (traces of $Ni_2L_3^+$).

Similarly, a CH_2Cl_2-solution of the same starting materials was stirred for 24 h under a N_2 atmosphere. ^{31}P-NMR (81.03 MHz, CH_2Cl_2/CD_2Cl_2): 64.0, 58.1 ($Ni_2L_3^+$); 66.3 (traces of NiL_2); 29.4 ($[Ph_2P(CH_2Cl)CH_2CH_2SBzl]Cl$).

Reaction of $Ni_2L_2Br_2$ with Et_3OBF_4. 12.75 mg (1.66×10^{-5} mol) $Ni_2L_2Br_2$ and 17 mg (8.9×10^{-4} mol) Et_3OBF_4 were dissolved under exclusion of air in CH_2Cl_2 in a 10 ml volumetric flask. Part of this solution was diluted to $[Ni_2L_2Br_2] = 8.6 \times 10^{-5}$M, and the VIS spectrum corresponded to that of unchanged $Ni_2L_2Br_2$. Addition of pyridine (1 drop) from a syringe in the cell caused a rapid color change from light red to brown. After a few hours, the VIS spectrum corresponds to that of pure $Ni_2L_3^+$, with $[Ni_2L_3^+] = 5.75 \times 10^{-5}$M.

The rest of the stock solution was treated with pyridine, stirred for 2 h and evaporated to dryness. ^{31}P-NMR (81.03 MHz, CH_2Cl_2/CD_2Cl_2): 64.0 (1P); 58.1 (2P).

Determination of the Stoichiometry of $Ni_2L_3^+$ by Job*'s Method.* For solubility reasons, CH_2Cl_2/acetone (4:1 by volume) was chosen as the solvent system. Samples of standard solutions of NiL_2 (3.94×10^{-4} mol dm^{-3}) and of $[Ni(H_2O)_6](ClO_4)_2$ (3.92×10^{-4} mol dm^{-3}) were weighed to make up the mole fractions indicated in *Fig. 1.* The absorbances of the mixtures were determined after 20 h at 375 nm.

Determination of the Equilibrium Composition of the System $[Ni_2L_3]Br \rightleftharpoons NiL_2 + 1/2\ Ni_2L_2Br_2$ in CH_2Cl_2/C_2H_5OH Mixtures. Two 10 ml aliquots of a CH_2Cl_2 stock solution containing NiL_2 and $Ni_2L_2Br_2$ in 1:2 ratio were pipetted into 100 ml volumetric flasks. The first was filled to the mark with CH_2Cl_2 and the second with EtOH. The ethanol containing solution was then evaporated to ≈ 20 ml to remove CH_2Cl_2 (b.p. 40°, EtOH b.p. 78.5°, azeotrope: b.p. $< 39.9°$, $> 95\%$ CH_2Cl_2 at 101 Pa). Further evaporation would have led to irreversible precipitation of NiL_2. The reduced volume was then complemented to 100 ml with EtOH. These two standard solutions were then weighed out and mixed to give the desired solvent mixtures in which the product ratios were determined approximately by spectrophotometry. The extinction coefficients of the three species are probably subject to some uncertainty for the different solvent mixtures. However, their values can not be checked independently from variation in the species concentration. For the calculation of the composition, we thus assumed them to remain the same. In fact, we have spectrophotometric evidence for the extrema of the graph, that $n_{Ni_2L_3} + = 0$ in CH_2Cl_2 and 1 in EtOH. Furthermore, the addition of bromide to an EtOH-solution of $[Ni_2L_3]ClO_4$ leaves the UV/VIS spectrum unchanged.

Kinetics. Equal amounts of pre-thermostated solutions were mixed rapidly and transferred into a thermostated quartz cell. The reactions were followed at 372 nm.

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