Part I. Description of X-ray data collection and structural solutions

X-ray Structural Determination of (dippe)Ni(η^2-C,S-thiophene) (2). **2** was dissolved in cold CH_2Cl_2, layered with hexanes and kept at -30 °C overnight. A single crystal of dimensions 0.03 x 0.03 x 0.40 mm^3 was mounted on a glass fiber with oil. Data were collected at -80 °C on a Siemens SMART CCD area detector system employing a 3kW sealed tube X-ray source operating at 2.0 kW. 1.3 hemispheres of data were collected over 13 h, yielding 12790 total data after integration using SAINT. Laue symmetry revealed an rhomohedral crystal system, and cell parameters were determined from 2561 unique reflections.[1] The space group was assigned as *R3c* on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 18 there are 3 independent molecules within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0479$ and $wR_2 = 0.0652$.[2]

X-ray Structural Determination of (dippe)Ni(η^2-C,S-benzothiophene) (4). **4** was dissolved in cold CH_2Cl_2, layered with hexanes and kept at -30 °C overnight. A single crystal of dimensions 0.01 x 0.14 x 0.18 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 1.3 over 13 h, yielding 10280 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 2495 unique reflections. The space group was assigned as *C2/c* on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 12 there are 3 independent molecules within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with

hydrogens included in idealized locations. The structure refined with final residuals of R_1 = 0.1058 and wR_2 = 0.2465.

X-ray Structural Determination of (dippe)$_2$Ni$_2$(benzothiophene) (5). Crystals of **5** were obtained by slow evaporation of hexanes. A single crystal of dimensions 0.35 x 0.42 x 0.50 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 20055 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 6219 unique reflections. The space group was assigned as $P2_1/n$ on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a Z value of 4 there is one independent molecules within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of R_1 = 0.0336 and wR_2 = 0.0766.

X-ray Structural Determination of (dippe)Ni(2,2'-biphenyl) (7). Crystals of **7** were obtained by layering a THF solution of **7** with hexanes and cooling to -30 °C. A single crystal of dimensions 0.08 x 0.26 x 0.28 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 28192 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 7941 unique reflections. The space group was assigned as $P2_1/n$ on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a Z value of 4 there is one molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of R_1 = 0.0497 and wR_2 = 0.0815.

X-ray Structural Determination of (dippe)$_2$Ni$_3$S$_2$(2,2'-biphenyl) (9). Crystals of **9** were obtained by standing a solution of **6** in benzene for 3 weeks. A single crystal of dimensions 0.20 x 0.20 x 0.40 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 28192 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 7941 unique reflections. The space group was assigned as *C2/c* on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 12 there is one and a half molecules within the asymmetric unit. Two molecules of benzene also crystallized on special positions in the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0504$ and $wR_2 = 0.1320$.

X-ray Structural Determination of dippe$_2$Ni (10). Crystals of **10** were obtained by slow evaporation of hexanes. A single crystal of dimensions 0.24 x 0.33 x 0.42 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 7983 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 2539 unique reflections. The space group was assigned as *C2/c* on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 4 there is one-half of a molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0444$ and $wR_2 = 0.1148$.

X-ray Structural Determination of (dippe)Ni(SH)$_2$ (11). Crystals of **11** were obtained by layering a CH_2Cl_2 solution of **11** with hexanes and cooling to -30 °C. A single crystal of

dimensions 0.25 x 0.28 x 0.30 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 11979 total data after integration using SAINT. Laue symmetry revealed an tetragonal crystal system, and cell parameters were determined from 3973 unique reflections. The space group was assigned as *I*-4 on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 8 there is one molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0379$ and $wR_2 = 0.0846$.

X-ray Structural Determination of (dippe)$_2$Ni$_2$(μ-S)(μ-H) (13). Crystals of **13** were obtained by cooling a pentane solution of **13** and **8** to -30 °C. A single crystal of dimensions 0.23 x 0.31 x 0.51 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 11136 total data after integration using SAINT. Laue symmetry revealed a triclinic crystal system, and cell parameters were determined from 6909 unique reflections. The space group was assigned as *P*1 on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 2 there is one molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. A bridging hydride ligand, located in a difference Fourier map, was included and refined isotropically. The structure refined with final residuals of $R_1 = 0.0310$ and $wR_2 = 0.0673$.

X-ray Structural Determination of (dippe)$_2$Ni$_3$S$_2$(C$_{13}$H$_{10}$) (15). Crystals of **15** were obtained by standing a solution of **15** in benzene for 2 weeks. A single crystal of dimensions 0.20 x 0.25 x 0.35 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 30198 total data after integration using SAINT. Laue symmetry revealed an

triclinic crystal system, and cell parameters were determined from 12380 unique reflections. The space group was assigned as *P*-1 on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 6 there are three molecules within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0820$ and $wR_2 = 0.2202$.

X-ray Structural Determination of (dippe)Ni(η^2-C,S-1,9-dimethyldibenzothiophene) (19). Crystals of **19** were obtained by layering a THF solution of **19** with hexanes and cooling to -30 °C. A single crystal of dimensions 0.20 x 0.20 x 0.35 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 14 h, yielding 12550 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 3461 unique reflections. The space group was assigned as $P2_1/c$ on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 4 there is one molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0824$ and $wR_2 = 0.2479$.

X-ray Structural Determination of (dippe)Ni(η^2-C,S-thioxanthene) (20). Crystals of **20** were obtained by layering a THF solution of **20** with hexanes and cooling to -30 °C. A single crystal of dimensions 0.20 x 0.20 x 0.30 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 15493 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 4686 unique reflections. The space group was assigned as $P2_1/c$ on the basis of systematic absences

using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 4 there is one molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0632$ and $wR_2 = 0.1039$.

X-ray Structural Determination of (dippe)Ni(η^2-C,S-thianthrene) (21). Crystals of **21** were obtained by layering a THF solution of **21** with hexanes and cooling to -30 °C. A single crystal of dimensions 0.20 x 0.30 x 0.40 mm^3 was mounted on a glass fiber with oil. Data were collected as above over 7 h, yielding 15702 total data after integration using SAINT. Laue symmetry revealed an monoclinic crystal system, and cell parameters were determined from 5124 unique reflections. The space group was assigned as $P2_1/c$ on the basis of systematic absences using XPREP, and the structure solved using direct methods included in the SHELXTL 5.04 package. For a *Z* value of 4 there is one molecule within the asymmetric unit. In the final model, non-hydrogen atoms were refined anisotropically (full matrix on F^2), with hydrogens included in idealized locations. The structure refined with final residuals of $R_1 = 0.0519$ and $wR_2 = 0.1125$.

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(1) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10x the listed values.((

(2) Using the SHELXTL 5.04 package, $R_1 = (\Sigma \| F_o | - | F_c \|) / \Sigma | F_o |$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2] \}^{½}$, where $w = 1/[\sigma^2(F_o^2) + (a \cdot P)^2 + b \cdot P]$ and $P = [f \cdot (\text{Maximum of 0 or } F_o^2) + (1-f) \cdot F_c^2]$.

Part II. ORTEP drawings of compounds with labeling scheme.

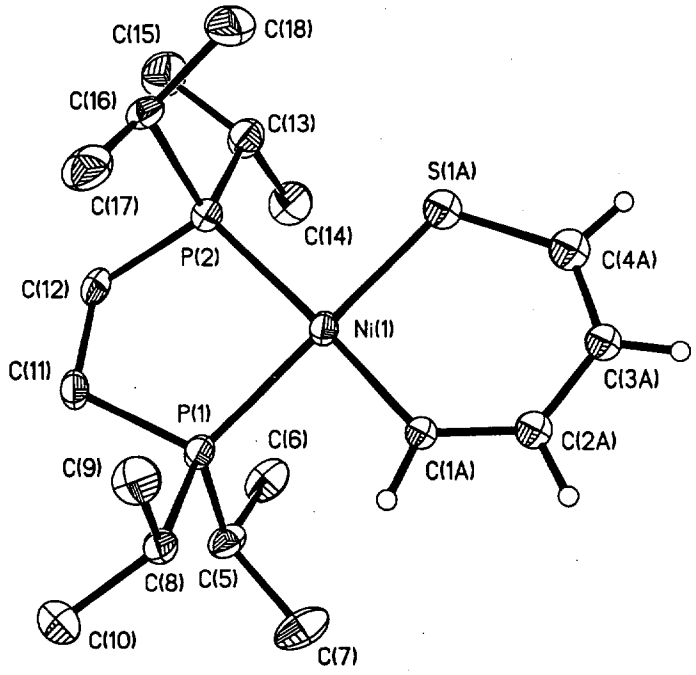

Figure 1. ORTEP drawing of (dippe)Ni(η^2-C,S-thiophene) **2**.