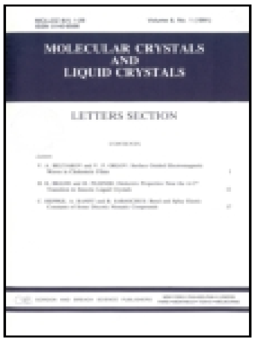

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# Synthesis and Crystal Structure of the Mononuclear Nickel Complex *[$Me_2CHN(PPh_2)_2$]$Ni(SCH_2Ph)_2$*

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*The mononuclear nickel complex [$Me_2CHN(PPh_2)_2$]$Ni(SCH_2Ph)_2$ has been synthesized by the reaction of [$Me_2CHN(PPh_2)_2$]$NiCl_2$ with $PhCH_2SH$ and $Et_3N$ in $CH_2Cl_2$ in 77% yield. The title complex was structurally characterized by $^1H$ NMR, $^{31}P\{^1H\}$ NMR spectroscopy as well as X-ray crystallography. The X-ray diffraction analysis reveals that the molecular structure consists of a central nickel atom coordinated by two phosphorus atoms of the bis(diphenylphosphanyl)amine and two sulfur atoms of benzylthiolate. There are no classical hydrogen bonds but van der Waals' interactions exist to stabilize the solid state in the crystal packing.*

**Keywords** Crystal structure; diphosphine ligand; mononuclear nickel; synthesis

## Introduction

Bis(diphenylphosphanyl)amine *R*N($PPh_2$)$_2$ have been widely utilized by synthetic chemists over past decades in coordination chemistry and inorganic chemistry because of their unique structures and novel properties.[1–5] Our recent published work reported a series of the mononuclear nickel complex with chelating bis(diphenylphosphanyl)amine and ethanedithiolate or propanedithiolate were successfully prepared and structurally characterized by spectroscopy and X-ray analysis.[6, 7] As a continuation of our studies on nickel complex, we have synthesized a new nickel complex by the condensation reaction. Herein, we present the synthesis and structural characterization of the mononuclear nickel complex [$Me_2CHN(PPh_2)_2$]$Ni(SCH_2Ph)_2$.

## Experimental

### *Synthesis of the Title Complex*

To a solution of [$Me_2CHN(PPh_2)_2$]$NiCl_2$ (0.1 mmol) and $PhCH_2SH$ (0.2 mmol) in $CH_2Cl_2$ (15 mL) was added $Et_3N$ (0.2 mmol) and the new mixture was stirred for 1 hr at room temperature. The solution was washed with $H_2O$ to remove $Et_3NHCl$ and then removal of

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**Table 1.** Crystal data and structure refinements details for the title complex

| | |
|---|---|
| Empirical formula | $C_{41}H_{41}NNiP_2S_2$ |
| Formula weight | 732.52 |
| Temperature (K) | 113(2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | P2(1)/*n* |
| *a* (Å) | 10.542(2) |
| *b* (Å) | 28.491(6) |
| *c* (Å) | 12.972(3) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 110.21(3) |
| $\gamma$ (°) | 90 |
| $V$ (Å$^3$) | 3656.1(13) |
| $Z$ | 4 |
| $D_{\text{calc}}$ (g·cm$^{-3}$) | 1.331 |
| $\mu$ (mm$^{-1}$) | 0.763 |
| $F(000)$ | 1536 |
| Crystal size (mm$^3$) | 0.20 × 0.18 × 0.12 |
| $\theta_{\min}$, $\theta_{\max}$ (°) | 1.43, 25.02 |
| Reflections collected/unique | 27,585/6447 |
| $R_{\text{int}}$ | 0.1445 |
| *hkl* range | $-12 \le h \le 12$<br>$-28 \le k \le 33$<br>$-15 \le l \le 15$ |
| Completeness to $\theta_{\max}$ (%) | 99.8 |
| Data/restraints/parameters | 6447/230/455 |
| Goodness of fit on $F^2$ | 1.106 |
| $R1/wR2$ $[I > 2\sigma(I)]$ | 0.1244/0.2612 |
| $R1/wR2$ (all data) | 0.1827/0.2982 |
| Largest diff peak and hole/e Å$^{-3}$ | 0.662/−0.659 |

the solvent afforded 0.056 g (77%) of the title complex as a black solid. $^1$H NMR (500 MHz, $CDCl_3$): 8.07 (*q*, $J = 6.5$ Hz, 8H, *o*-PPhH), 7.52 (*t*, $J = 7.2$ Hz, 4H, *p*-PPhH), 7.45 (*t*, $J = 7.2$ Hz, 8H, *m*-PPhH), 7.09 (*d*, $J = 7.0$ Hz, 4H, *o*-PhH), 7.03 (*t*, $J = 7.2$ Hz, 4H, *m*-PhH), 6.97 (*t*, $J = 7.0$ Hz, 2H, *p*-PhH), 3.36 (*s*, 4H, $2SCH_2$), 3.39–3.29 (*m*, 1H, NCH), and 0.55 [*d*, $J = 7.0$ Hz, 6H, $NCH(CH_3)_2$] ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% $H_3PO_4$): 56.57 (s) ppm.

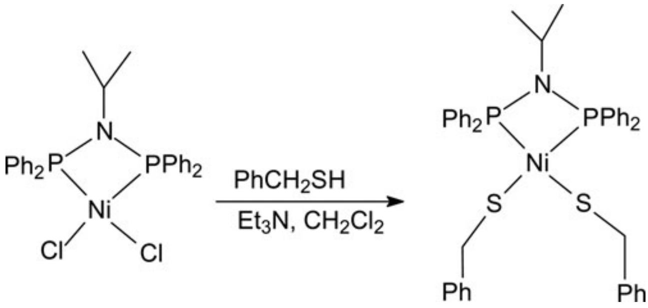
### *X-Ray Structure Determination*

Single crystals of the title complex suitable for X-ray diffraction analysis were grown by slow evaporation of $CH_2Cl_2$/hexane solutions at 4°C. A single crystal of the title complex was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 K by using a graphite monochromator with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) in the

$\omega$-$\phi$ scanning mode. Data collection, reduction, and absorption correction were performed by *CRYSTALCLEAR* program.[8] The structure was solved by direct methods using the SHELXS-97 program[9] and refined by full-matrix least-squares techniques SHELXL-97[10] on $F^2$. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

## Results and Discussion

The synthetic strategy for the title complex was shown in Scheme 1. That is, treatment of the nickel dichloride complex $[Me_2CHN(PPh_2)_2]NiCl_2$ and two equivalents of $PhCH_2SH$ with $Et_3N$ resulted in the formation of the title complex in 77% yield. The title complex is air-stable red solid and soluble in $CH_2Cl_2$, which has been characterized by $^1$H NMR and $^{31}P\{^1H\}$ NMR spectroscopy.



**Scheme 1.** Synthesis of the title complex.

The $^1$H NMR spectra showed a quadruplet at $\delta$ 8.07 ppm and two triplets at $\delta$ 7.52 ppm and $\delta$ 7.45 ppm for the phenyl protons of the diphenylphosphanyl groups and a doublet at $\delta$ 7.09 ppm and two triplet at $\delta$ 7.03 ppm and $\delta$ 6.97 ppm for the phenyl protons of the benzyl groups. The $^{31}P\{^1H\}$ NMR spectra displayed a singlet at $\delta$ 56.57 ppm, consistent with the corresponding values of the coordinated diphosphine ligands,[11–13] for the two phosphorus atoms of $Me_2CHN(PPh_2)_2$ chelated to the nickel atom.

The molecular structure of the title complex has been determined by single crystal X-ray diffraction analysis. While the ORTEP and packing views are shown in Figs. 1 and 2, the selected bond lengths and angles are presented in Table 2, respectively. The title complex crystallizes in monoclinic space group P2(1)/*n* with four molecules in the unit cell and one molecule in the asymmetric unit. As shown in Fig. 1, the molecular structure consists of a distorted square-planar nickel coordinated with two phosphorus atom of $Me_2CHN(PPh_2)_2$ and two sulfur atoms of benzylthiolate. The plan Ni1P1N1P2 is almost coplanar with the mean deviation of 0.0025 Å. The dihedral angle between the plans Ni1P1N1P2 and Ni1S1S2 is 179.5°. It should be noted that the sum of the bond angle around Ni1 atom is 360.01°, indicating the coplanar property of the Ni1, P1, P2, S1, and S2 atoms. The bond lengths [Ni(1)–P(1) = 2.141(3) Å, Ni(1)–S(1) = 2.179(3) Å, P(1)–N(1) = 1.703(7) Å, S(1)–C(1) = 1.862(10) Å] and the bond angles [P(1)–Ni(1)–P(2) = 73.54(10)°, S(1)–Ni(1)–S(2) = 94.76(11)°, P(1)–N(1)–P(2) = 97.6(3)°] are consistent with other compounds.[14–18]

As shown in Fig. 2, the crystal packing diagram shows van der Waals' interactions stabilize the solid state of the title complex.

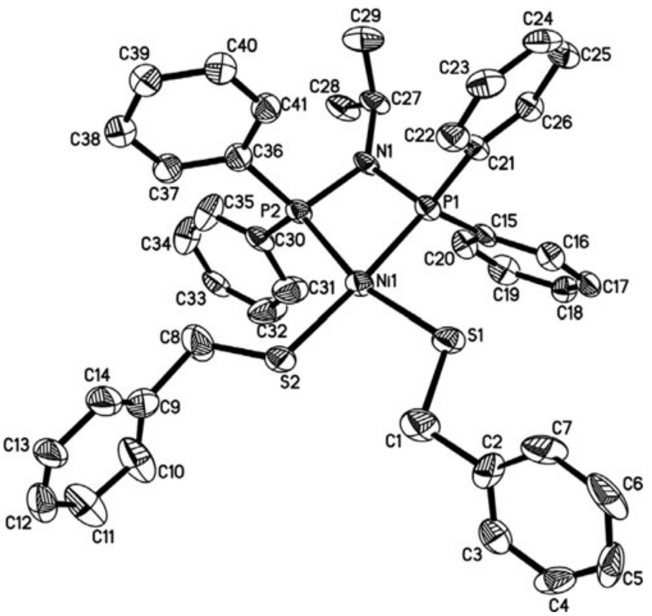


**Figure 1.** ORTEP view of the title complex with 30% probability level ellipsoids.

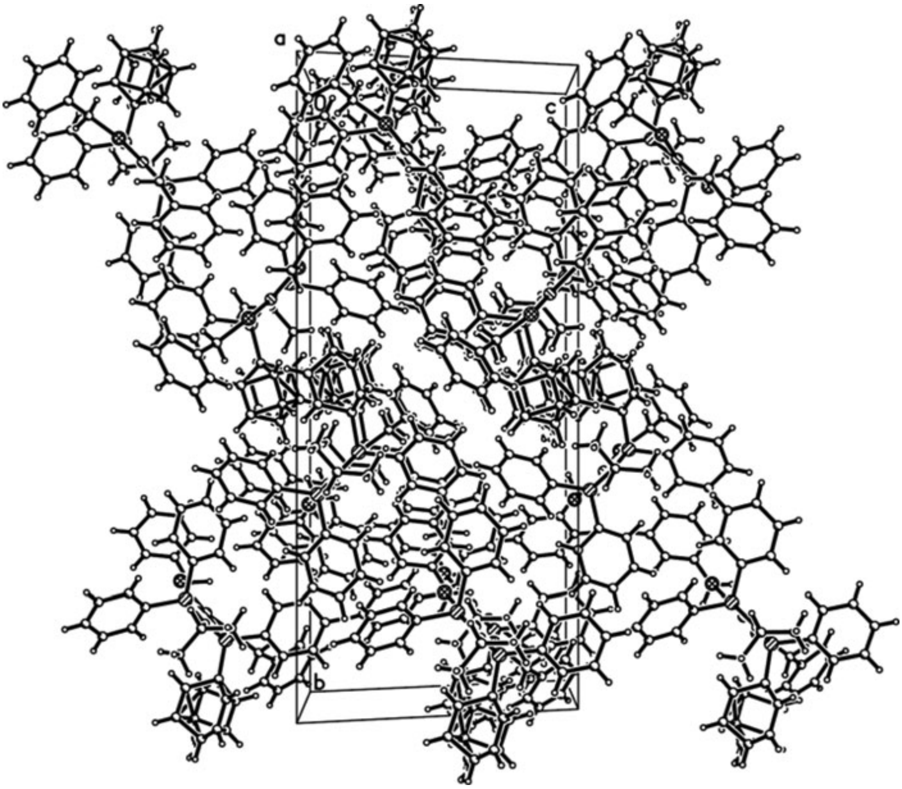


**Figure 2.** Crystal packing diagram of the title complex.

**Table 2.** Selected bond lengths (Å) and angles (°) for the title complex

| | | | |
|---|---|---|---|
| Ni(1)–P(1) | 2.141(3) | Ni(1)–P(2) | 2.164(3) |
| Ni(1)–S(1) | 2.179(3) | Ni(1)–S(2) | 2.181(3) |
| P(1)–N(1) | 1.703(7) | P(2)–N(1) | 1.722(7) |
| S(1)–C(1) | 1.862(10) | S(2)–C(8) | 1.825(14) |
| N(1)–C(27) | 1.489(10) | C(1)–C(2) | 1.523(14) |
| P(1)–Ni(1)–P(2) | 73.54(10) | P(1)–Ni(1)–S(1) | 89.60(11) |
| P(2)–Ni(1)–S(1) | 163.13(11) | P(1)–Ni(1)–S(2) | 175.63(11) |
| P(2)–Ni(1)–S(2) | 102.11(11) | S(1)–Ni(1)–S(2) | 94.76(11) |
| N(1)–P(1)–Ni(1) | 95.1(2) | N(1)–P(2)–Ni(1) | 93.7(3) |
| C(27)–N(1)–P(1) | 127.7(6) | C(27)–N(1)–P(2) | 134.6(6) |
| P(1)–N(1)–P(2) | 97.6(3) | C(1)–S(1)–Ni(1) | 111.2(4) |

## Conclusion

In summary, the title complex [$Me_2CHN(PPh_2)_2$]$Ni(SCH_2Ph)_2$ has been successfully prepared and structurally characterized by X-ray crystallography.

## Acknowledgments

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## Supplemental Data

CCDC 1041540 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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