

Cyclometalation of Thiobenzophenones with Mononuclear Methyiron and -cobalt Complexes

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Keywords: C–H activation / Cyclometalation / Cobalt / Iron / Nickel / S ligands

Under smooth conditions (–70 °C) thiobenzophenone derivatives react with $[\text{Fe}(\text{CH}_3)_2(\text{PMe}_3)_4]$ to form five-membered metallacycles **1** and **2** by C–H activation. These complexes show octahedral coordination geometry; with $[\text{Co}(\text{CH}_3)_2(\text{PMe}_3)_4]$, complexes **3** and **4** with trigonal-bipyramidal coordination are formed. Reaction with basic $[\text{Ni}(\text{CH}_3)_2(\text{PMe}_3)_3]$ causes reductive elimination (of ethane) with formation of

zerovalent $\eta^2\text{-C}=\text{S}$ complexes **5** and **6**, possessing triangular-planar coordination. The structures of the complexes were confirmed by X-ray diffraction, and their coordination geometry is discussed.

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Introduction

Stoichiometric and catalytic transformations involving C–H activations are of special interest in synthetic chemistry, especially for an easy functionalization of specific bonds.

In comparison to 4d and 5d transition metals, the availability of cobalt and iron compounds provides a new and low-cost route to metallation reactions initiated by C–H bond activation. At this stage it is interesting that little is known about this type of reactive intermediates.

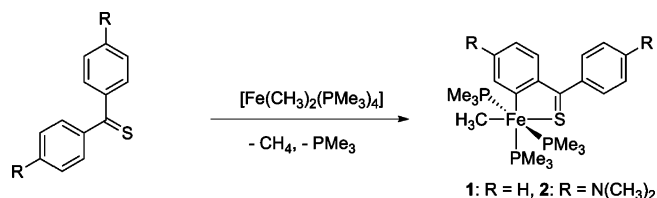
Cyclometalation reactions are known for almost all transition metals, and typically a pre-coordination of an anchoring group which contains a donor atom N, P, O or S (S-donating ones restricted to thioether and thiolato groups) is assumed.^[1–2]

Likewise, reactions and catalytic functionalizations of benzophenones have been already studied.^[3] However, for such homologous thiobenzophenones, there are until now only few examples described in the literature.^[4–6] Thiobenzophenones with only one anchoring group form just an end-on C=S coordination or bridge metal centers (Os),^[7] allow an η^2 -coordination (Pt, V, Ti),^[8] or lead to a heterolytic C=S bond breaking (Mo).^[9]

Results and Discussion

We describe here for the first time cyclometalation reactions, under mild conditions, of thiobenzophenones by C–H activation at mononuclear iron and cobalt centers.

When combining the starting materials in diethyl ether (Scheme 1) at –70 °C, according to the procedure described in the Experimental Section, an immediate change of color from red to green is observed, accompanied by gas evolution (CH_4).



Scheme 1. Reaction of thiobenzophenones with $\text{Fe}(\text{CH}_3)_2(\text{PMe}_3)_4$.

Green hexagonal crystals are obtained from pentane solutions at –27 °C with a yield of 78% (**2**: green, rhombic crystals, 81% yield).

The ^1H NMR spectroscopic data for **1** shows a characteristic resonance of the FeCH_3 group at $\delta = 0.54$ ppm (3 H) split to a broad triplet ($^3J_{\text{P,H}} = 11.8$ Hz), whereas the coupling with the *cis*-disposed trimethylphosphane ligand collapses by reversible dissociation.

The carbon and C=S metallation is demonstrated by characteristic chemical shifts observed in the ^{13}C NMR spectra for C (**1**: $\delta = 195.4$ ppm; **2**: $\delta = 193.4$ ppm) and for the C=S function (**1**: $\delta = 163.9$ ppm; **2**: $\delta = 156.4$ ppm).

The molecular structure of **1** (Figure 1) shows an octahedrally coordinated iron center with three meridionally disposed P-donors. The other three ligand positions are occu-

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pied by the metallated C-atom, the S-donor atom and the methyl group (C1) *trans* to the sulfur atom. The bond lengths of the iron atoms to the two *trans*-oriented P-atoms are 2.242 and 2.246 Å; they are almost identical, and only in the Fe1–P2 distance (2.269 Å) is the *trans* influence of the metallated carbon atom C2 noticed. The significantly different Fe–C bond lengths [Fe1–C1 2.106 Å, Fe1–C2 2.022(4) Å] are attributed to the different carbon hybridizations (sp^3 -C and sp^2 -C).^[10] The C8–S1 bond of 1.675(4) Å is slightly shorter than that found in free thiobenzophenone (1.635 Å)^[11] and confirms the double-bond character of the C=S bond. In contrast, thiolato complexes of cobalt exhibit typical bond lengths in a range between 1.80–1.85 Å for the C–S single bond.^[12]

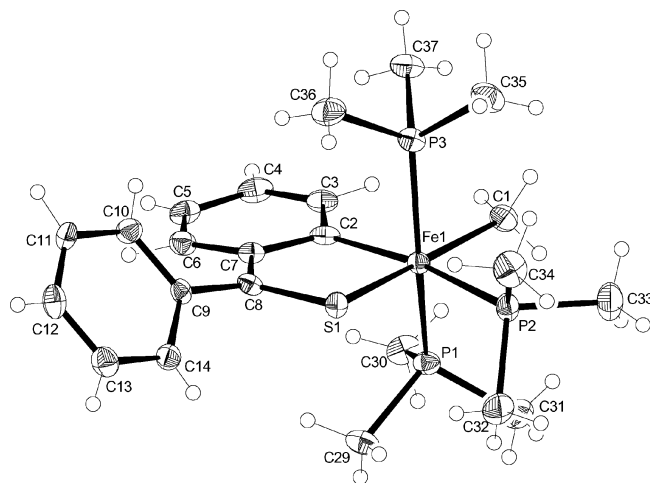
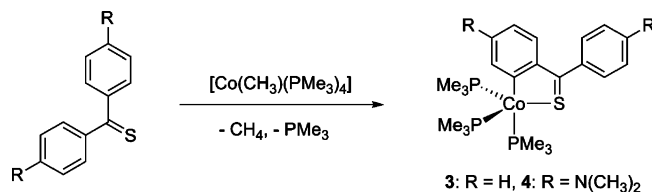


Figure 1. Molecular structure of **1**; selected distances [Å] and angles [°]: Fe1–C1 2.106(5), Fe1–C2 2.022(4), Fe1–S1 2.168(37), Fe1–P1 2.246(19), Fe1–P2 2.269(22), Fe1–P3 2.242(18), C8–S1 1.675(4); C2–Fe1–S1 83.87(12), C1–Fe1–S1 175.37(15), P3–Fe1–P1 158.34(5), C2–Fe1–P2 168.54(12), C1–Fe1–P2 91.69(15), P3–Fe1–P2 100.06(5), P1–Fe1–P2 95.29(5).

Under analogous experimental conditions with the methylcobalt compound (Scheme 2), the cyclometalation of thiobenzophenones occurs with similar reaction rates (120 min), without a significant effect caused by the substituent [R = H, N(CH₃)₂].



Scheme 2. Reaction of thiobenzophenones with Co(CH₃)(PMe₃)₄.

In comparison with free thiobenzophenone, presenting a chemical shift at δ = 230.0 ppm in ¹³C NMR spectrum, the C=S function of the newly coordinated complex exhibits an intense high-field shift of approx. 60 ppm (**3**: δ = 167.6 ppm; **4**: δ = 171.1 ppm).

The molecular configuration of **3** is confirmed by X-ray crystal structure determination (Figure 2). The coordination geometry can be described as trigonal-bipyramidal

[C1–Co1–P3 169.50(9)°] with three phosphorus nuclei in equatorial and axial positions. The coordination sphere is completed by the metallated carbon atom C1 (axial) and the S-donor (equatorial) which attacks the cobalt center with a bite angle of [C1–Co1–S1 84.53(9)°]. The measured C=S bond length of 1.688(3) Å is similar to that of **1**.

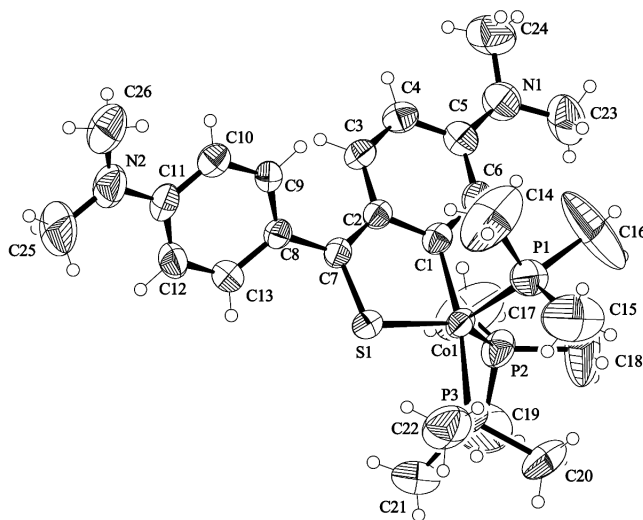
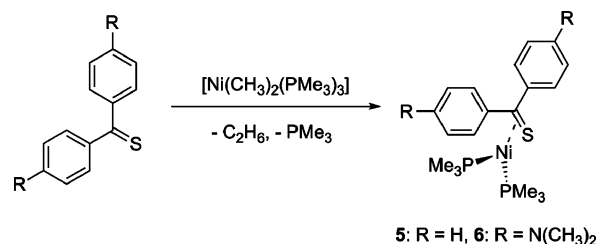


Figure 2. Molecular structure of **4**; selected distances [Å] and angles [°]: Co1–C1 1.965(3), Co1–S1 2.1510(9), Co1–P1 2.1940(10), Co1–P2 2.2196(10), Co1–P3 2.2203(10), C7–S1 1.688(3); C1–Co1–S1 84.53(9), C1–Co1–P3 169.50(9), C1–Co1–P1 87.11(9), S1–Co1–P1 112.86(4), C1–Co1–P2 92.12(9), S1–Co1–P2 132.87(4), P1–Co1–P2 113.89(4).

When basic Ni(CH₃)₂(PMe₃)₃ is used under analogous experimental conditions, the reductive elimination prevails against the C–H activation (Scheme 3).



Scheme 3. Reaction of thiobenzophenones with Ni(CH₃)₂(PMe₃)₃.

The orange-brown crystals of **6** obtained from a pentane solution at –27 °C are extremely air-sensitive and melt at 92 °C with decomposition (**5**: yellow powder, dec. > 97–99 °C).

The loss of both nickel-bound methyl substituents can be confirmed by the NMR spectra of **5** and **6**, and the multiplicities of the signals reveal the high symmetry of the molecule, which is confirmed by an X-ray structure analysis of **6**.

The molecular structure of **6** (Figure 3) shows a triangular-planar coordination geometry with two P-ligand atoms and the midpoint of the η^2 -C=S coordination [Ni–

S 2.1289 Å and Ni C 2.020(2) Å] in-plane attached to the zerovalent nickel atom. The C=S bond is with 1.769(2) Å, as expected, longer than in **1** and **4**, which corresponds to the aforementioned η^2 -C=S platinum complex.^[8]

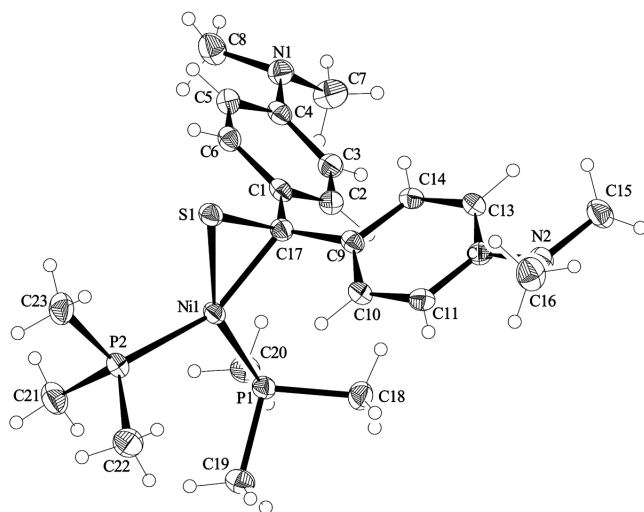


Figure 3. Molecular structure of **6**; selected distances [Å] and angles [°]: Ni1–C17 2.020(2), Ni1–S1 2.1289(8), Ni1–P1 2.1510(9), Ni1–P2 2.1817(8), C17–S1 1.769(2); P1–Ni1–P2 105.66(3), C17–S1–Ni1 61.60(7), C17–Ni1–P1 102.01(6), S1–Ni1–P1 152.35(2), C17–Ni1–P2 152.30(6).

Conclusions

We have shown that, under mild conditions, the cyclometalation of thiobenzophenones by C–H activation of 3d transition metals was realized by using iron and cobalt centers. The rate of cyclometalation appears to be independent of the *para* substituent [R = H or N(CH₃)₂] and the metal (Fe, Co).

The synthesized complexes are model compounds which are related with suggested ruthenium intermediates of the first step in the catalytic cycle for the C–C coupling of benzophenones. Furthermore, as the iron and cobalt centers retain their low oxidation states with similar effect of donor atoms after the reaction, it should be possible to perform a second C–H activation. A subsequent elimination step accompanied with a C–C coupling would facilitate a catalytic reaction sequence. Experiments with this aim are the subject of current investigations.

Experimental Section

General Procedure: Solutions of [Fe(CH₃)₂(PMe₃)₄]^[13] [CoCH₃(PMe₃)₄]^[14] or [Ni(CH₃)₂(PMe₃)₃]^[15] in diethyl ether (50 mL) on a scale of about 1–2 mmol were combined with equimolar amounts of the thiobenzophenones in the same solvent (50 mL) and the mixtures stirred at –70 °C. The reaction mixture was warmed up to 20 °C and stirred for another 120 min (maximum). The volatiles were removed in vacuo, and the residue was extracted with pentane through a glass-sinter disc (G3). Crystals formed upon cooling of the solution to –27 °C. Decantation, wash-

ing with ice-cold pentane and drying in vacuo afforded analytically pure substances **1–6**.

1: Yield 865 mg (78%), m.p. 112–114 °C. IR (Nujol): $\tilde{\nu}$ = 1601 (m, ν C=C), 1570 (m, ν C=C), 1513 (m, ν FeC=C), 943 (vs, ρ_1 PCH₃) cm^{–1}. ¹H NMR (500 MHz, [D₈]thf, 300 K): δ = 0.54 (t, ³*J*_{PH} = 11.8 Hz, 3 H, FeCH₃), 0.60 (s, 18 H, PCH₃), 1.51 (s, 9 H, PCH₃), 6.76 (t, ³*J*_{H,H} = 6.8 Hz, 1 H, CH), 7.22 (t, ³*J*_{H,H} = 7.0 Hz, 1 H, CH), 7.22 (t, ³*J*_{H,H} = 7.0 Hz, 1 H, CH), 7.29–7.33 (m, 3 H, Ar-H), 7.68 (d, ⁴*J*_{PH} = 4.6 Hz, 1 H, CH), 7.75 (d, ³*J*_{H,H} = 7.9 Hz, 2 H, CH), 7.89 (d, ³*J*_{H,H} = 7.5 Hz, 1 H, CH) ppm. ¹³C NMR (125 MHz, [D₈]thf, 300 K): δ = –7.6 (m, FeCH₃), 17.1 (t', ¹*J*_{PC} + ³*J*_{PC} = 10.8 Hz, PCH₃), 20.0 (d, ¹*J*_{PC} = 6.6 Hz, CH₂), 119.9 (s, CH), 122.3 (s, CH), 123.9 (s, CH), 125.5 (s, CH), 128.1 (s, CH), 147.0 (s, CH), 147.7 (s, C), 158.7 (s, C), 163.9 (s, C=S), 195.4 (s, FeC) ppm. ³¹P NMR (202 MHz, [D₈]thf, 296 K): δ = 10.2 (br. s, 2 P, PCH₃), –63.4 (br. m, 1 P, PCH₃) ppm. C₂₆H₃₈FeNP₃ (513.3): calcd. C 60.83, H 7.46, N 2.73, P 18.10; found C 60.62, H 7.15, N 2.78, P 18.21.

2: Yield 803 mg (81%), m.p. (dec.) 106–108 °C. IR (Nujol): $\tilde{\nu}$ = 1602 (m, ν C=C), 1573 (m, ν C=C), 1517 (m, ν FeC=C), 943 (vs, ρ_1 PCH₃) cm^{–1}. ¹H NMR (300 MHz, [D₈]thf, 300 K): δ = 0.06 (t, ³*J*_{PH} = 9.3 Hz, 3 H, FeCH₃), 0.71 (s, 18 H, PCH₃), 1.25 (s, 9 H, PCH₃), 2.35 (s, 6 H, NCH₃), 2.56 (s, 6 H, NCH₃), 6.46 (d, ³*J*_{H,H} = 8.5 Hz, 1 H, CH), 6.51 (d, ³*J*_{H,H} = 8.7 Hz, 2 H, CH), 7.53 (d, ⁴*J*_{H,H} = 2.7 Hz, 1 H, CH), 7.75 (d, ³*J*_{H,H} = 8.7 Hz, 2 H, CH), 8.06 (d, ³*J*_{H,H} = 9.3 Hz, 1 H, CH) ppm. ¹³C NMR (125 MHz, [D₈]thf, 300 K): δ = –5.8 (t, ²*J*_{PC} = 24.7 Hz FeCH₃), 15.5 (t', ¹*J*_{PC} + ³*J*_{PC} = 13.5 Hz, PCH₃), 17.9 (m, PCH₃), 39.8 (s, NCH₃), 40.0 (s, NCH₃), 107.2 (s, CH), 112.1 (s, CH), 121.9 (s, CH), 125.8 (s, CH), 129.0 (s, CH), 130.3 (s, 1 C), 135.1 (s, 1 C), 146.4 (s, 1 C), 151.3 (s, 1 C), 156.4 (s, C=S), 193.4 (s, FeC) ppm. ³¹P NMR (121.5 MHz, [D₈]thf, 296 K): δ = 17.8 (br. s, 1 P, PCH₃), 14.8 (br. s, 2 P, PCH₃) ppm. C₂₇H₄₉FeN₂P₃S (582.5): calcd. C 55.67, H 8.40, N 4.81, S 5.50; found C 56.43, H 9.63, N 4.52, S 5.54.

3: Yield 540 mg (67%), m.p. 106–108 °C. IR (Nujol): $\tilde{\nu}$ = 1599 (m, ν C=C), 1580 (m, ν C=C), 1519 (m, ν CoC=C), 945 (vs, ρ_1 PCH₃) cm^{–1}. ¹H NMR (300 MHz, [D₈]thf, 300 K): δ = 1.28 (br. s, 27 H, PCH₃), 6.75 (br. s, 1 H, CH), 7.14 (br. s, 2 H, CH), 7.34 (br. s, 2 H, CH), 7.84 (br. s, 2 H, CH), 8.06 (br. s, 1 H, CH), 8.45 (br. s, 1 H, CH) ppm. ¹³C NMR (125 MHz, [D₈]thf, 300 K): δ = 20.4 (d, ¹*J*_{PC} = 18.5 Hz, PCH₃), 114.9 (d, ⁵*J*_{PC} = 4.3 Hz, CH), 119.1 (s, CH), 120.2 (s, CH), 122.2 (s, CH), 123.0 (s, CH), 127.3 (s, CH), 148.8 (d, ⁴*J*_{PC} = 6.1 Hz, 1 C), 157.6 (s, 1 C), 167.6 (m, C=S), 175.3 (m, CoC) ppm. ³¹P NMR (202 MHz, [D₈]thf, 296 K): δ = 22.3 (br. s, 3 P, PCH₃) ppm. C₂₂H₃₆CoP₃S (484.4): calcd. C 54.55, H 7.49, P 19.18; found C 53.45, H 7.53, P 18.33.

4: Yield 427 mg (45%), m.p. (dec.) 120–122 °C. IR (Nujol): $\tilde{\nu}$ = 1601 (m, ν C=C), 1570 (m, ν C=C), 1515 (m, ν CoC=C), 941 (vs, ρ_1 PCH₃) cm^{–1}. ¹H NMR (500 MHz, [D₈]thf, 296 K): δ = 1.17 (br. s, 27 H, PCH₃), 2.37 (s, 6 H, NCH₃), 2.61 (s, 6 H, NCH₃), 6.42 (d, ³*J*_{H,H} = 8.2 Hz, 1 H, CH), 6.55 (d, ³*J*_{H,H} = 8.5 Hz, 2 H, CH), 7.45 (d, ⁴*J*_{H,H} = 2.5 Hz, 1 H, CH), 7.66 (d, ³*J*_{H,H} = 8.5 Hz, 2 H, CH), 8.01 (d, ³*J*_{H,H} = 8.5 Hz, 1 H, CH) ppm. ¹³C NMR (121.5 MHz, [D₈]thf, 296 K): δ = 20.4 (td, ¹*J*_{PC} = 22.5, ³*J*_{PC} = 3.7 Hz PCH₃), 40.4 (s, NCH₃), 41.1 (s, NCH₃), 110.9 (s, CH), 113.7 (s, CH), 123.6 (s, CH), 126.3 (s, CH), 130.7 (s, CH), 132.4 (s, 1 C), 133.3 (s, 1 C), 141.7 (s, 1 C), 151.8 (s, 1 C), 171.1 (s, C=S), 175.3 (s, CoC) ppm. ³¹P NMR (202 MHz, [D₈]thf, 296 K): δ = 17.1 (br. s, 3 P, PCH₃) ppm. C₂₆H₄₆CoN₂P₃S (570.58): calcd. C 54.73, H 8.13, N 4.91, S 5.62; found C 54.23, H 8.55, N 4.77, S 5.67.

5: Yield 493 mg (71%), m.p. (dec.) 92–94 °C. IR (Nujol): $\tilde{\nu}$ = 1575 (m, ν C=C), 923 (vs, ρ_1 PCH₃) cm^{–1}. ¹H NMR (300 MHz, [D₈]thf, 296 K): δ = 0.90 (br. s, 18 H, PCH₃), 6.65 (d, ³*J*_{H,H} = 8.7 Hz, 4 H,

Table 1. Crystal data for **1**, **4** and **6**.

	1	4	6
Empirical formula	C ₂₀ H ₄₀ FeP ₃ S	C ₂₆ H ₄₆ CoN ₂ P ₃ S	C ₂₃ H ₃₈ N ₂ NiP ₂ S
Formula mass	461.34	570.55	495.26
Crystal size [mm]	0.12 × 0.17 × 0.5	0.10 × 0.12 × 0.28	0.10 × 0.35 × 0.50
Crystal system	triclinic	orthorhombic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.113(12)	10.7517(9)	8.2490(16)
<i>b</i> [Å]	14.8030(13)	16.4595(14)	11.846(2)
<i>c</i> [Å]	19.9730(12)	17.2354(15)	14.354(3)
α [°]	102.80(2)	90	99.24(3)
β [°]	98.04(2)	90	103.24(3)
γ [°]	101.11(2)	90	107.51(3)
<i>V</i> [Å ³]	2530.8(5)	3050.1(5)	1261.7(4)
<i>Z</i>	4	4	2
<i>D</i> _{calcd.} [g/cm ³]	1.211	1.242	1.304
μ (Mo- <i>K</i> α) [mm ⁻¹]	0.870	0.805	0.991
Temperature [K]	293(2)	293(2)	293(2)
Data collection range [°]	2.8 ≤ 2 θ ≤ 54	3.4 ≤ 2 θ ≤ 50	3.0 ≤ 2 θ ≤ 54
<i>h</i>	−11 ≤ <i>h</i> ≤ 11	−12 ≤ <i>h</i> ≤ 12	−10 ≤ <i>h</i> ≤ 9
<i>k</i>	−18 ≤ <i>k</i> ≤ 18	−19 ≤ <i>k</i> ≤ 19	−15 ≤ <i>k</i> ≤ 10
<i>l</i>	−25 ≤ <i>l</i> ≤ 24	−20 ≤ <i>l</i> ≤ 14	−18 ≤ <i>l</i> ≤ 18
Number of reflections measured	32783	16139	4447
Number of unique data	10810 (<i>R</i> _{int} = 0.081)	5403 (<i>R</i> _{int} = 0.027)	3609 (<i>R</i> _{int} = 0.043)
Parameters	793	298	304
<i>GoF</i> on <i>F</i> ²	1.162	1.021	0.970
<i>R</i> ₁ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0557	0.0364	0.0287
<i>wR</i> ₂ (all data)	0.1311	0.0964	0.1081

CH), 8.06 (d, ³*J*_{H,H} = 8.7 Hz, 4 H, CH) ppm. ¹³C NMR (125 MHz, [D₈]thf, 296 K): δ = 17.5 (m, PCH₃), 18.3 (m, PCH₃), 112.3 (s, CH), 130.4 (s, CH), 141.7 (s, 1 C), 147.9 (s, NC), 154.3 (s, C=S) ppm. ³¹P NMR (202 MHz, [D₈]thf, 296 K): δ = 1.7 (br. s, 2 P, PCH₃) ppm. C₁₉H₂₈NiP₂S (409.13): calcd. C 55.78, H 6.90, P 15.14; found C 55.34, H 7.31, P 15.18.

6: Yield 310 mg (56%), m.p. (dec.) 97–99 °C. IR (Nujol): $\tilde{\nu}$ = 1581 (m, ν C=C), 925 (vs, ρ_1 PCH₃) cm⁻¹. ¹H NMR (300 MHz, [D₆]benzene, 296 K): δ = 0.77 (br. s, 9 H, PCH₃), 1.01 (br. s, 9 H, PCH₃), 2.56 (s, 12 H, NCH₃), 6.65 (d, ³*J*_{H,H} = 8.7 Hz, 4 H, CH), 8.06 (d, ³*J*_{H,H} = 8.7 Hz, 4 H, CH) ppm. ¹³C NMR (125 MHz, [D₆]benzene, 296 K): δ = 17.5 (m, PCH₃), 18.3 (m, PCH₃), 112.3 (s, CH), 130.4 (s, CH), 141.7 (s, 1 C), 147.9 (s, NC), 152.2 (s, C=S) ppm. ³¹P NMR (202 MHz, [D₆]benzene, 296 K): δ = −0.4 (br. s, 1 P, PCH₃), 0.9 (br. s, 1 P, PCH₃) ppm. C₂₃H₃₈N₂NiP₂S (495.3): calcd. C 55.78, H 7.73, N 5.66, S 6.47; found C 55.53, H 8.41, N 5.77, S 5.73.

Crystal Structure Analysis: Crystal data are presented in Table 1. Data collections were performed with a STOE IPDSII image-plate detector using Mo-*K* α radiation (λ = 0.71019 Å). Details of the crystal structures are given in Table 1. Data collection: Stoe X-Area.^[16] Cell refinement: Stoe X-Area.^[16] Data reduction: Stoe X-RED.^[16] The structure was solved by direct methods with SHELXS-97,^[17] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on *F*² using SHELXL-97.^[17] In the title compounds, the hydrogen atoms on C were placed at calculated positions (C–H: 0.93 Å for CH groups and 0.96 Å for methyl groups) and were allowed to ride on the parent atom [*U*_{iso}(H) = 1.2 *U*(C) for CH groups and *U*_{iso}(H) = 1.5 *U*(C) for methyl groups]. CCDC-678969 for (for **1**), -678970 (for **4**) and -678971 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Financial support of this work by the Fonds der Chemischen Industrie is gratefully acknowledged. R. B. thanks the China Postdoctoral Science Foundation and the Shandong University Postdoctoral Science Foundation and Innovation.

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Received: April 18, 2008
Published Online: June 19, 2008