Dichlorodinickel(I) Complexes with μ^2-CO or μ^2-CS Bridges and Trimethylphosphane Ligands: Homologous Composition, but Different Frameworks[**]

Hans-Friedrich Klein,* Andreas Schmidt,
Ulrich Flörke, and Hans-Jürgen Haupt*

It has long been known that reduction of metal halides in the absence of suitable supporting ligands results in cluster formation if metal–metal bonds and/or additional ligand bridges can be formed.[1] In the first steps of such condensation reactions highly reactive dinuclear intermediates with low coordination numbers of metals in low oxidation states play an important role. Starting with nickel in the presence of trimethylphosphane and an appropriate source of carbonyl or thiocarbonyl ligands, we have found conditions which lie on the border of metal deposition and allow the isolation und characterization of coordinatively unsaturated dinickel compounds in the formal oxidation state + I.

At $-80\,^{\circ}$C in the absence of coordinating solvents, [Ni(cod)(PMe$_3$)$_2$] (cod = 1,5-cyclopentadiene) reacts with oxalyl chloride according to Equation (1) to give a violet solution which is stable at 20 °C. Addition of pentane and cooling led to precipitation of black crystals of **1**.[2]

$$3\,[\mathrm{Ni(cod)(PMe_3)_2}] + (\mathrm{COCl})_2 \xrightarrow[-80\,^{\circ}\mathrm{C}]{\text{toluene}} \underset{\mathbf{1}}{[\mathrm{Ni_2Cl_2(CO)(PMe_3)_3}]} + [\mathrm{Ni(CO)(PMe_3)_3}] + 3\,\mathrm{cod} \qquad (1)$$

Complex **1** dissolves readily in diethyl ether or THF to give a deep blue solution. However, the clear solutions in THF deposit a brown solid after 30 min at 20 °C, and after 3 h [Ni(CO)(PMe$_3$)$_3$] and NiCl$_2$ are found as main products. Solutions in diethyl ether or toluene are more stable and afford single crystals on cooling.

Parallel to the carbonyl complex **1**, we obtained the thiocarbonyldinickel complex **2** of analogous composition which, however, differs substantially from **1** with respect to chemical properties and structure. At $-80\,^{\circ}$C in the absence of coordinating solvents [Ni(cod)(PMe$_3$)$_2$] reacts with thiophosgene according to Equation (2) to give a red solution which is stable at 20 °C and produces a red oil on evaporation. Within a few hours or after some days, the oily phase forms shiny black needles of the toluene solvate $\mathbf{2}\cdot\mathrm{C_7H_8}$. Under diethyl ether **2** forms a sparingly soluble red oil. Clear solutions in THF are stable up to 70 °C, in contrast to the carbonyl compound **1**.

$$[\mathrm{Ni(cod)(PMe_3)_2}] + \mathrm{CSCl_2} \xrightarrow[-80\,^{\circ}\mathrm{C}]{\text{toluene}} \underset{\mathbf{2}}{[\mathrm{Ni_2Cl_2(CS)(PMe_3)_3}]} + \mathrm{cod} + \ldots \qquad (2)$$

The molecular structure of **1**[3] (Figure 1) consists of a hook-shaped backbone of two nickel and two chlorine atoms in a plane which also accommodates the μ^2-CO ligand and, at the corner of the hook (Ni1-Ni2-Cl2 99.34(7)°), one of the three P donor atoms. The remaining trimethylphosphane ligands are perpendicularly coordinated to Ni1. Disregarding the Ni–Ni interaction, one of the metal centers (Ni1) has an approximately square-planar coordination geometry, and the second (Ni2) a T-shaped environment. The angles within the T piece (Cl2-Ni2-C1 155.1(2)°, Ni2-C1-O1 159.2(6)°) are consistent with a highly unsymmetrical carbonyl bridge (semibridging mode), while the bridge angle Ni2-C1-Ni1 78.3(3)° leads to an Ni–Ni contact (2.3634(14) Å) in the region of a single bond, which is shorter than those reported for comparable dinickel complexes (2.439(1)–2.694(1) Å).[4] The central bonding in the molecule may be described by a metal–metal bond of the donor–acceptor type and/or a three-center, two-electron bridge bond.

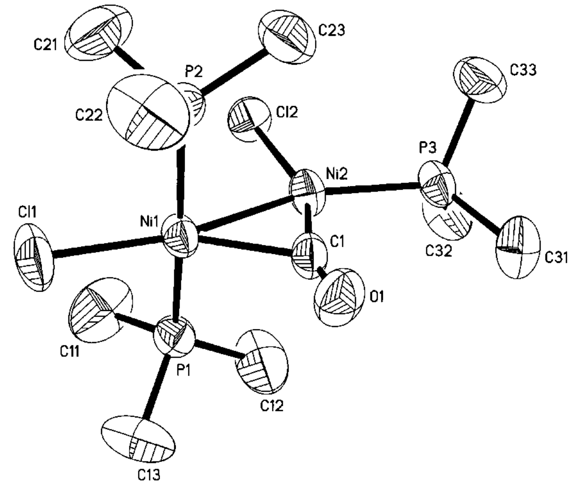

Figure 1. Molecular structure of **1**; selected bond lengths [Å] and angles [°]: Ni1–Ni2 2.3642(14), Ni1–C1 1.999(6), Ni2–C1 1.730(8), Ni1–P1 2.212(2), Ni1–P2 2.215 (2), Ni2–P3 2.169(2), Ni1–Cl1 2.223(2), Ni2–Cl2 2.252(2), C1–O1 1.167(8); C1-Ni1-P1 93.2(2), C1-Ni1-P2 91.1(2), C1-Ni2-P3 103.5(2), P1-Ni1-P2 168.70(8), C1-Ni1-Ni2 45.8(2), C1-Ni2-Ni1 55.9(2), C1-Ni1-Cl1 150.3(2), C1-Ni2-Cl2 155.1(2), P3-Ni2-Ni1 159.37(7), Cl1-Ni1-Ni2 163.98(9), Cl2-Ni2-Ni1 99.34(7), P1-Ni1-Ni2 86.93(6), P2-Ni1-Ni2 88.59(6), P3-Ni2-Cl2 101.26(8), P1-Ni1-Cl1 90.73(8), P2-Ni1-Cl1 90.71(8), O1-C1-Ni1 122.3(5), O1-C1-Ni2 159.2(6), Ni1-C1-Ni2 78.3(3).

While the bridging carbonyl ligand of **1** is represented in the IR spectrum by a strong ν(CO) band at 1830 cm^{-1}, which lies well within the range of terminal CO ligands and is in accord with an almost linear Ni2-C1-O1 angle, the fingerprint region of the spectrum down to 400 cm^{-1} displays the few absorptions typical for coordinated trimethylphosphane but without the expected band splitting.[5] In the ^{1}H, ^{13}C, and ^{31}P NMR spectra (298–230 K) singlet resonances for trimethylphosphane are observed. At first sight these findings are inconsistent with the low molecular symmetry (Figure 1). Broadening and splitting of the ^{31}P signals (2:1, $\Delta\delta = 1.2$), which is independent of dilution, begin only at $-80\,^{\circ}$C. This indicates extraordinarily high mobility of the ligands.[6] To obtain a time-averaged

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[*] Prof. Dr. H.-F. Klein, Dipl.-Ing. A. Schmidt
Institut für Anorganische Chemie der Technischen Universität
Petersenstrasse 18, D-64287 Darmstadt (Germany)
Fax: (+49) 6151-164173
E-mail: hfklein@hrz2.hrz.tu-darmstadt.de
Prof. Dr. H.-J. Haupt, Dr. U. Flörke
Anorganische und Analytische Chemie der Universität-GH
Warburger Strasse 100, D-33095 Paderborn (Germany)

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molecular C_{2v} symmetry in the atomic framework $Ni_2Cl_2COP_3$ on the NMR time scale, both metal centers must exchange their coordination geometries by shifting the CO bridge and by intramolecular migration of all other ligands. A schematic trajectory for the process is shown in Figure 2.

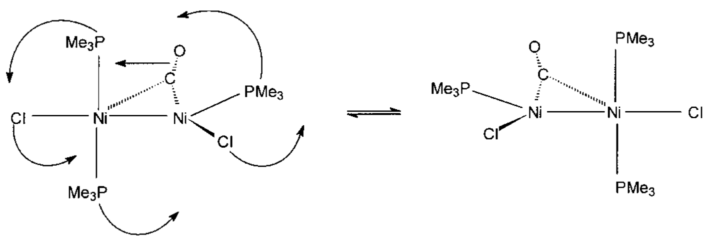


Figure 2. Intramolecular ligand migrations in **1**.

In contrast to the hook-shaped Cl-Ni-Ni-Cl framework of **1**, the structure of **2**[7] (Figure 3) contains a roof-shaped Cl-Ni-Ni-Cl unit with a dihedral angle Cl1-Ni1-Ni2-Cl2 of 125.1°. A symmetrically bridging trimethylphosphonio-μ^2-(CS) ligand is attached to the roof perpendicular to the Ni–Ni vector. The other two trimethylphosphane groups are coordinated to the ends of the dinickel unit in a transoid configuration. As the bridge angles (Ni2-C1-Ni1 91.5(3)°, Ni2-S1-Ni1 77.10(7)°) do not allow for a bonding Ni–Ni interaction (Ni1–Ni2 2.7169(14) Å), coordination of both metal centers can be described as quasitetrahedral. The ^{1}H NMR spectrum (298–230 K) contains a doublet for the phosphonio group and two doublets for the trimethylphosphane ligands.

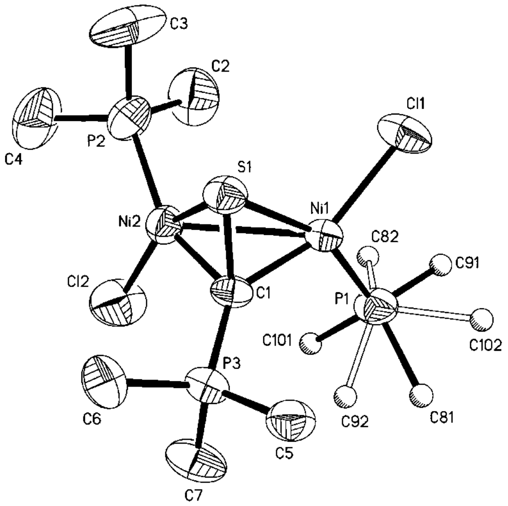
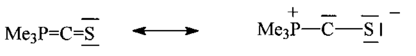


Figure 3. Molecular structure of **2**; selected bond lengths [Å] and angles [°]: Ni1–C1 1.874(7), Ni2–C1 1.918(7), Ni1–P1 2.149(2), Ni2–P2 2.179(3), Ni1–S1 2.201(2), Ni2–S1 2.158(2), Ni1–Cl1 2.205(2), Ni2–Cl2 2.187(3), Ni1–Ni2 2.7169(14), S1–C1 1.743(7), C1–P3 1.736(7); C1-Ni1-P1 107.0(2), C1-Ni1-S1 49.9(2), P1-Ni1-S1 156.43(10), C1-Ni1-Cl1 156.7(2), P1-Ni1-Cl1 95.99(9), S1-Ni1-Cl1 106.89(9), C1-Ni1-Ni2 44.9(2), P1-Ni1-Ni2 111.66(8), S1-Ni1-Ni2 50.74(6), Cl1-Ni1-Ni2 122.56(8), C1-Ni2-S1 50.2(2), C1-Ni2-P2 154.7(2), S1-Ni2-P2 107.76(10), C1-Ni2-Cl2 104.0(2), S1-Ni2-Cl2 152.71(11), P2-Ni2-Cl2 99.31(11), C1-Ni2-Ni1 43.6(2), S1-Ni2-Ni1 52.17(6), P2-Ni2-Ni1 115.32(8), Cl2-Ni2-Ni1 118.36(9), C1-S1-Ni2 57.7(2), C1-S1-Ni1 55.3(2), Ni2-S1-Ni1 77.10(7), P3-C1-S1 122.0(4), P3-C1-Ni1 138.2(4), S1-C1-Ni1 74.9(3), P3-C1-Ni2 129.1(4), S1-C1-Ni2 72.1(3), Ni1-C1-Ni2 91.5(3).

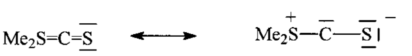
By reaction with methyllithium, which with **1** under the mildest conditions invariably leads to a deposition of elemental nickel, **2** is transformed into the novel dimethyldinickel compound **3** [Eq. (3)].

$$2 + 2\,\mathrm{LiMe} \rightarrow \underset{\mathbf{3}}{[\mathrm{Ni_2Me_2(CS)(PMe_3)_3}]} + 2\,\mathrm{LiCl} \qquad (3)$$

Brown crystals which are thermally stable up to 84 °C were obtained from pentane. Spectroscopic data in solution closely resemble those of **2** apart from the expected effects of higher electron density. Therefore, **3** is likely to arise from a substitution of the chloride ligands with retention of the remaining atomic framework. The dinuclear complexes **2** and **3** coordinate and stabilize one of the smallest representatives of the so-far unknown thiocarbonylphosphoranes **A**. As in the isoelectronic thiocarbonyl systems **B**[8] and **C**,[9, 10] the dipolar resonance form is favored by μ^2-C,μ^2-S coordination perpendicular to the metal–metal vector (six-electron donor) and is largely independent of the bond angles in the bridge.



A



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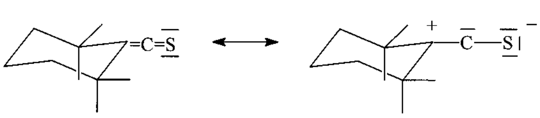

C

In contrast to **2** the NMR spectra of **3** suggest either a cisoid arrangement of methylnickel groups or fast exchange of ligands in solution gives the appearence of molecular C_s symmetry.

Experimental Section

1: Solutions of $[Ni(cod)(PMe_3)_2]$ (7.78 g, 24.4 mmol) in 80 mL of toluene and of oxalyl chloride (1.03 g, 8.11 mmol) in 30 mL of toluene were mixed at −80 °C. A yellow-brown color developed that, after warming to 20 °C, changed to violet. The solution was filtered, 70 mL of pentane was added, and the solution was kept at −27 °C for 14 h. The crystalline product was recrystallized from 400 mL of diethyl ether at −27 °C to give shiny black crystals; yield 1.57 g (44% with respect to oxalyl chloride), m.p. 153–155 °C (decomp); elemental analysis: calcd: C 27.03, H 6.12, Ni 26.41, P 20.90; found: C 27.35, H 5.88, Ni 26.35, P 20.86; ^{1}H NMR (200 MHz, $[D_8]$toluene, 25 °C, TMS): $\delta = 1.39$ (s); ^{1}H NMR (200 MHz, $[D_8]$toluene/CD_2Cl_2, −80 °C, TMS): $\delta = 1.08$ (s, 9H, PCH_3), 1.36 (s, 18H, PCH_3); ^{13}C NMR (75.4 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 13.9$ (s, PCH_3); ^{31}P NMR (81 MHz, CD_2Cl_2, 25 °C, H_3PO_4): $\delta = -14.9$ (s); ^{31}P NMR (81 MHz, $[D_8]$toluene /CD_2Cl_2, −80 °C, H_3PO_4): $\delta = -0.8$ (s, 1P), 0.4 (s, 2P).

2: Solutions of $[Ni(cod)(PMe_3)_2]$ (4.00 g, 12.5 mmol) in 40 mL of toluene and of freshly condensed thiophosgene (0.66 g, 5.70 mmol) in 30 mL of toluene were combined at −80 °C with vigorous stirring. The color changed from brown to red within a few minutes. After warming to 20 °C, the mixture was stirred for 1 h and filtered. Reducing the volume of the filtrate in vacuo afforded a red oil, which spontaneously crystallized within three days. Recrystallization from toluene at −70 °C afforded black needles of **2**·

C_7H_8; yield 1.15 g (36% with respect to thiophosgene), m.p. 88–90°C, elemental analysis: calcd: C 36.94, H 6.38%, P 16.81; found: C 37.08, H 6.55, P 16.81; ^{1}H NMR (200 MHz, [D$_6$]acetone, 25°C, TMS): $\delta = 1.28$ (d, ^2J(P,H) = 7.4 Hz, 9H, PCH_3), 1.42 (d, ^2J(P,H) = 9.2 Hz, 9H, PCH_3), 1.98 (d, ^2J(P,H) = 13.7 Hz, 9H, $^+PCH_3$), 2.30 (s, 3H, CCH_3), 7.17 (m, 5H, CH); ^{31}P NMR (81 MHz, [D$_6$]acetone, 25°C, H_3PO_4): $\delta = -9.9$ (d, ^3J(P,P) = 9 Hz, 1P, PCH_3), −4.5 (s, 1P, PCH_3), 26.9 (s, ^3J(P,P) = 9 Hz, 1P, $^+PCH_3$).

3: To a solution of **2** (1.45 g, 2.62 mmol) in 40 mL of THF was added a solution of methyllithium in diethyl ether (3.3 mL, 1.6 M, 5.3 mmol) at −80°C with vigorous stirring The mixture turned light brown. Removing the volatile materials in vacuo, extracting the residue with 50 mL of pentane, and cooling to −27°C for 10 h gave brown crystals; yield 0.68 g (62%); m.p. 84–88°C (decomp), elemental analysis calcd for $C_{12}H_{33}Cl_2Ni_2P_3S$ (419.8): C 34.36, H 7.92, P 22.14; found C 34.33, H 7.86, P 22.10; ^{1}H NMR (200 MHz, [D$_8$]THF, 25°C, TMS): $\delta = -0.78$ (s, 6H, $NiCH_3$), 1.18 (d, ^2J(P,H) = 6.3 Hz, 18H, PCH_3), 1.66 (d, ^2J(P,H) = 12.9 Hz, 9H, $^+PCH_3$); ^{13}C NMR (75.4 MHz, [D$_8$]THF, 25°C, TMS): $\delta = -24.1$ (s, $NiCH_3$), 15.5 (d, ^1J(P,C) = 55.7 Hz, $^+PCH_3$), 17.0 (d, ^1J(P,C) = 9.5 Hz, PCH_3); ^{31}P NMR (81 MHz, [D$_8$]THF, 25°C, H_3PO_4): $\delta = -4.8$ (s, PCH_3), 23.1 (s, $^+PCH_3$).

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[2] In toluene **1** is also obtained by treating [$NiCl_2(PMe_3)_2$] with [$Fe_2(C_5H_5)_2(CO)_3(\mu\text{-}SnMe_2)$] or $Na_2[Fe(CO)_4] \cdot 1.5$dioxane in 15% and 28% yield, respectively.

[3] Crystal data for **1**: $C_{10}H_{27}Cl_2Ni_2OP_3$, $M_r = 444.6$; crystal dimensions: $0.55 \times 0.45 \times 0.15$, monoclinic, space group $P2_1/c$, $a = 10.902(3)$, $b = 16.923(4)$, $c = 12.323(3)$ Å, $\beta = 115.05(2)°$, $V = 2059(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.434$ g cm^{-3}, $F(000) = 920$; 4611 reflections with $4.8 < 2\Theta < 55.0°$, Siemens R3 diffractometer, $Mo_{K\alpha}$ radiation ($\mu = 2.309$ mm^{-1}), graphite monochromator. The structure was solved with direct methods (SHELXTL V5), refinement with 4413 independent reflections ($R_{int} = 0.0344$) for 173 parameters against $|F^2|$ with SHELXTL V5 gave $R = 0.063$, $wR2 = 0.192$ (all data); max./min. residual electron density 1.143/−0.531 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions.[7b]

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[5] Strong sharp bands were registered at 737 (ν_{as}(PC)) and 671 cm^{-1} (ν_s(PC)).

[6] A nickel complex in which two chelating $(Ph_2P)_2CH_2$ ligands are attached to a related atomic framework (μ-CO)Ni_2Cl_2 also shows fluxional behavior.[4]

[7] a) Crystal data for **2**: $C_{10}H_{27}Cl_2Ni_2P_3S \cdot C_7H_8$, $M_r = 552.7$; crystal dimensions: $0.30 \times 0.22 \times 0.20$ mm, monoclinic, space group $P2_1/n$, $a = 11.572(2)$, $b = 9.229(1)$, $c = 25.949(4)$ Å, $\beta = 99.10(1)°$, $V = 2736.4(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.342$ g cm^{-3}, $F(000) = 1152$; 6440 reflections with $5.4 < 2\Theta < 55.1°$, Siemens R3 diffractometer, $Mo_{K\alpha}$ radiation ($\mu = 1.824$ mm^{-1}), graphite monochromator. The structure was solved by direct methods (SHELXTL V5), refinement of 6308 independent reflections ($R_{int} = 0.0445$) for 224 parameters against $|F^2|$ with SHELXTL V5 gave $R1 = 0.063$, $wR2 = 0.171$ (all data); max./min. residual electron density 0.599/−0.424 e Å^{-3}. All non-hydrogen atoms except for the C atoms at P1 were refined anisotropically. Atoms C8–C10 were refined on split positions with mutual half occupation at a fixed distance d(PC). Hydrogen atoms were fixed at calculated positions. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-101260 and -101267. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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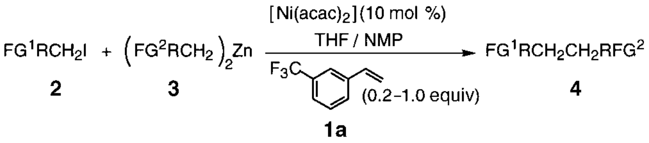
An Efficient Nickel-Catalyzed Cross-Coupling Between sp^3 Carbon Centers

Riccardo Giovannini, Thomas Stüdemann, Gaelle Dussin, and Paul Knochel*

The cross-coupling reaction between an organometallic species and an organic halide is an important method for forming a new carbon–carbon bond. Whereas transition metal catalyzed cross-coupling reactions between sp^2 carbon centers are well established[1] and routinely applied even in complex syntheses,[2] the cross-coupling reaction between two sp^3 carbon centers often requires the use of stoichiometric amounts of organocuprates,[3] which has several drawbacks. A nontransferred or nontransferable functional group is often wasted, and the moderate functional group diversity of lithium or magnesium cuprates[4] often limits their application. Recently, we have shown that the presence of a double bond in the position γ to the carbon–halogen bond considerably facilitates the reductive-elimination step of the cross-coupling.[5] The remote double bond coordinates to the nickel center and in this way removes electron density from the metal atom.[6] Although it is mechanistically interesting, the required presence of the double bond in the iodoalkane reduces the synthetic scope of the reaction. Herein, we report that the addition of catalytic amounts of an unsaturated additive such as **1a** allows an efficient [Ni(acac)$_2$]-catalyzed cross-coupling reaction to be performed between various polyfunctional organic halides **2** and diorganozinc compounds **3** to give the cross-coupling products **4** (Scheme 1); this considerably extends the scope of the reaction.



Scheme 1. Cross-coupling between sp^3 carbon centers in the presence of cocatalysts **1a**. FG = functional group; NMP = *N*-methylpyrrolidone.

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[*] Prof. Dr. P. Knochel, Dr. R. Giovannini, Dr. T. Stüdemann,
Dipl.-Ing. G. Dussin
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: (+49) 6421-28-2189
E-mail: knochel@ps1515.chemie.uni-marburg.de

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