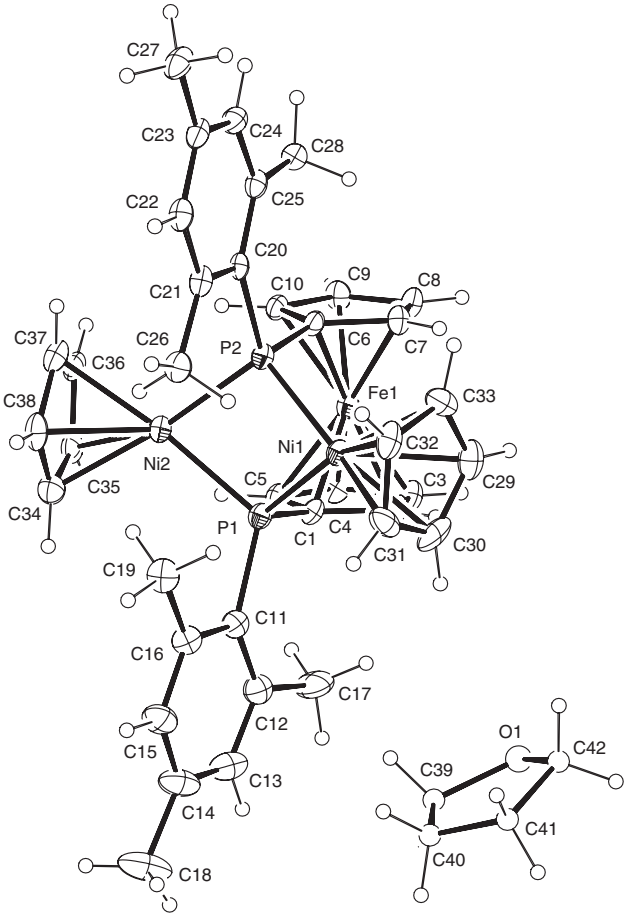
Christina Langen, Clemens Bruhn and Ulrich Siemeling*

Synthesis and crystal structure of μ-[1,1′-di(mesitylphosphanido) ferrocene]bis[η^5-cyclopentadienylnickel(II)] tetrahydrofurane solvate, $C_{42}H_{48}FeNi_2OP_2$



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Abstract

$C_{42}H_{48}FeNi_2OP_2$, orthorhombic, *Pbca* (no. 61), $a = 9.4551(4)$ Å, $b = 19.7133(9)$ Å, $c = 39.693(2)$ Å, $V = 7398.4(6)$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0598$, $wR_{ref}(F^2) = 0.1481$, $T = 100(2)$ K.

***Corresponding author: Ulrich Siemeling,** Institut für Chemie, Universität Kassel, Heinrich-Plett-Strasse 40, D-34132 Kassel, Germany, e-mail: siemeling@uni-kassel.de
Christina Langen and Clemens Bruhn: Institut für Chemie, Universität Kassel, Heinrich-Plett-Strasse 40, D-34132 Kassel, Germany

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Plate, brown
Size:	0.18 × 0.06 × 0.02 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.51 mm^{-1}
Diffractometer, scan mode:	STOE IPDS 2, ω-rotation
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20670, 6881, 0.085
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3905
$N(param)_{refined}$:	439
Programs:	Stoe & Cie [1], SHELX [2, 3], ORTEP [4]

Source of materials

All reactions involving air-sensitive compounds were performed in an inert atmosphere (argon or dinitrogen) by using standard Schlenk techniques or a conventional glovebox. Nickelocene [5] and 1,1′-di(mesitylphosphanyl)ferrocene [6, 7] were synthesized according to known procedures. THF (5 mL) was added to nickelocene (110 mg, 0.58 mmol) and 1,1′-di(mesitylphosphanyl)ferrocene (141 mg, 0.29 mmol) placed in a thick-walled ampoule. The reaction vessel was sealed and the mixture heated at 70 °C bath temperature with stirring for 4 days. The mixture was cooled to room temperature. Volatile components were removed under vacuum. The residue was extracted with *n*-hexane (5 mL) and insoluble material removed by filtration. The filtrate was reduced to dryness under vacuum, which afforded the product as an essentially air-stable dark brown solid. Yield = 198 mg (93%). Crystals of the title compound were obtained from a THF solution by slow evaporation at room temperature. **^{13}C NMR** (125.7 MHz, 295 K, C_6D_6): δ = 141.3 ($C_6H_2Me_3$), 137.2 ($C_6H_2Me_3$), 131.3 (m, $C_6H_2Me_3$), 91.6 (C_5H_5), 82.4 (C_5H_4P), 70.5 (C_5H_4P), 26.6 (m, *o*-Me), 21.0 ppm (*p*-Me). **^{31}P NMR**

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.6869(7)	0.3291(3)	0.12533(16)	0.0295(14)
C2	0.7262(7)	0.3918(3)	0.13952(16)	0.0319(15)
H2A	0.820220	0.408134	0.141978	0.038*
C3	0.6013(7)	0.4265(3)	0.14953(18)	0.0375(16)
H3A	0.596712	0.470265	0.159518	0.045*
C4	0.4847(7)	0.3839(3)	0.14188(17)	0.0357(16)
H4A	0.388051	0.393950	0.146034	0.043*
C5	0.5370(6)	0.3241(3)	0.12711(16)	0.0304(14)
H5A	0.481774	0.286770	0.119601	0.037*
C6	0.7211(6)	0.2575(3)	0.19756(15)	0.0281(13)
C7	0.7583(7)	0.3210(3)	0.21264(16)	0.0332(15)
H7A	0.851197	0.339072	0.214435	0.040*
C8	0.6337(7)	0.3522(3)	0.22434(17)	0.0327(15)
H8A	0.628582	0.394760	0.235478	0.039*
C9	0.5180(7)	0.3101(3)	0.21689(16)	0.0339(15)
H9A	0.421769	0.319384	0.221959	0.041*
C10	0.5700(7)	0.2512(3)	0.20045(15)	0.0300(14)
H10A	0.514715	0.214060	0.192725	0.036*
C11	0.8420(7)	0.2702(3)	0.06701(16)	0.0341(15)
C12	0.7924(7)	0.3223(4)	0.04628(18)	0.0408(17)
C13	0.8166(8)	0.3184(4)	0.0117(2)	0.053(2)
H13A	0.779390	0.353202	−0.002303	0.064*
C14	0.8906(8)	0.2674(5)	−0.00302(18)	0.055(2)
C15	0.9477(8)	0.2177(4)	0.01763(18)	0.0483(19)
H15A	1.003315	0.182744	0.007888	0.058*
C16	0.9255(7)	0.2179(3)	0.05223(17)	0.0364(16)
C17	0.7158(11)	0.3850(4)	0.0581(2)	0.063(2)
H17A	0.774895	0.409303	0.074427	0.076*
H17B	0.626525	0.371893	0.068839	0.076*
H17C	0.696281	0.414513	0.038816	0.076*
C18	0.9108(12)	0.2631(6)	−0.0406(2)	0.090(3)
H18A	0.874546	0.304506	−0.051142	0.108*
H18B	0.859229	0.223742	−0.049325	0.108*
H18C	1.011678	0.258225	−0.045651	0.108*
C19	0.9950(8)	0.1624(4)	0.07200(18)	0.0439(17)
H19A	0.922943	0.136862	0.084434	0.053*
H19B	1.062693	0.182119	0.087921	0.053*
H19C	1.044857	0.131768	0.056582	0.053*
C20	0.9117(6)	0.1372(3)	0.20250(15)	0.0266(13)
C21	1.0086(7)	0.0917(3)	0.18845(17)	0.0320(14)
C22	1.0707(7)	0.0412(3)	0.20844(17)	0.0339(15)
H22A	1.136775	0.011073	0.198412	0.041*
C23	1.0392(7)	0.0339(3)	0.24219(17)	0.0343(16)
C24	0.9412(7)	0.0781(3)	0.25579(17)	0.0331(15)
H24A	0.916127	0.073003	0.278832	0.040*
C25	0.8771(7)	0.1302(3)	0.23714(16)	0.0309(14)
C26	1.0502(7)	0.0934(3)	0.15180(17)	0.0349(15)
H26A	1.092272	0.137597	0.146500	0.042*
H26B	0.966151	0.086386	0.137779	0.042*
H26C	1.119170	0.057465	0.147298	0.042*
C27	1.1113(7)	−0.0190(3)	0.26310(18)	0.0430(18)
H27A	1.201585	−0.001141	0.271403	0.052*
H27B	1.128717	−0.059407	0.249338	0.052*
H27C	1.050963	−0.031030	0.282260	0.052*
C28	0.7743(7)	0.1728(3)	0.25665(16)	0.0344(15)
H28C	0.767883	0.155803	0.279807	0.041*
H28B	0.680945	0.170367	0.245979	0.041*
H28A	0.806841	0.219960	0.256913	0.041*
C29	1.0914(7)	0.3594(4)	0.1649(2)	0.0456(19)
H29A	1.050526	0.397763	0.175685	0.055*
C30	1.1072(7)	0.3507(4)	0.1304(2)	0.053(2)
H30A	1.073814	0.380243	0.113305	0.063*
C31	1.1829(7)	0.2890(4)	0.12560(17)	0.0463(19)
H31A	1.212364	0.270933	0.104546	0.056*
C32	1.2060(7)	0.2603(4)	0.15650(19)	0.0421(17)
H32A	1.254192	0.218899	0.160888	0.050*
C33	1.1444(7)	0.3039(4)	0.18063(17)	0.0418(18)
H33A	1.140599	0.295605	0.204190	0.050*
C34	0.6196(8)	0.1134(4)	0.09101(18)	0.0435(18)
H34A	0.637084	0.126802	0.068402	0.052*
C35	0.5073(7)	0.1378(3)	0.11203(17)	0.0378(16)
H35A	0.434805	0.168546	0.105562	0.045*
C36	0.5240(7)	0.1084(3)	0.14362(18)	0.0363(16)
H36A	0.464475	0.115129	0.162608	0.044*
C37	0.6465(7)	0.0665(3)	0.14239(19)	0.0401(17)
H37A	0.685807	0.042591	0.160942	0.048*
C38	0.6996(7)	0.0661(4)	0.10949(19)	0.0408(17)
H38A	0.775201	0.039060	0.101216	0.049*
P1	0.80712(17)	0.26101(8)	0.11295(4)	0.0286(4)
P2	0.83757(17)	0.20210(8)	0.17382(4)	0.0272(4)
Fe1	0.62291(9)	0.33525(4)	0.17378(2)	0.0291(2)
Ni1	0.98543(8)	0.26810(4)	0.14730(2)	0.0273(2)
Ni2	0.71711(8)	0.16512(4)	0.13086(2)	0.0288(2)
O1	1.136(2)	0.4931(6)	0.0589(5)	0.256(10)
C42	1.295(3)	0.4913(13)	0.0627(4)	0.223(14)
H42A	1.333513	0.537902	0.063953	0.268*
H42B	1.321849	0.466403	0.083349	0.268*
C40	1.234(2)	0.4220(11)	0.0149(4)	0.232(14)
H40A	1.232527	0.435301	−0.009113	0.278*
H40B	1.245990	0.372201	0.016306	0.278*
C39	1.1132(16)	0.4403(10)	0.0298(6)	0.219(12)
H39A	1.066423	0.399481	0.039084	0.263*
H39B	1.049278	0.460253	0.012678	0.263*
C41	1.3477(18)	0.456(2)	0.0323(8)	0.33(2)
H41A	1.392545	0.489109	0.016913	0.397*
H41B	1.420193	0.422196	0.038874	0.397*

(202.3 MHz, 295 K, C_6D_6): $\delta = -129.7$ ppm. HRMS/ESI(+): $m/z = 730.0634$ $[M]^+$, 730.0662 calcd. for $C_{38}H_{40}FeP_2Ni_2$

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

We recently investigated the reaction of 1,1′-ferrocenediyl-bridged secondary diphosphines of the type [Fe{μ^5-C_5H_4(PHR)}$_2$}] with two equivalents of nickelocene [8].

The reaction proceeds *via* intermediate mononuclear phosphido-phosphino chelates of the type [NiCp{Fe[η^5-C_5H_4(PR)][η^5-C_5H_4(PHR)]}] (Cp = η^5-cyclopentadienyl) and finally affords dinuclear nickel diphosphido complexes of the type [(NiCp)$_2${μ-Fe[η^5-C_5H_4(PR)]$_2$}]. The title complex was obtained as a pure substance from the corresponding reaction of [Fe{η^5-C_5H_4(PHMes)}$_2$] (Mes = mesityl). The intermediate [NiCp{Fe[η^5-C_5H_4(PMes)][η^5-C_5H_4(PHMes)]}] was evident from the characteristic ^{31}P NMR signals of this chelate due to the phosphido and the phosphino P atom respectively located at δ = −16.0 (s) and −32.7 ppm (d, $^1J_{PH}$ = 352 Hz) in C_6D_6 solution. [(NiCp)$_2${μ-Fe[η^5-C_5H_4(PMes)]$_2$}] is only the third structurally characterized compound of its kind. The molecular structure of this mesityl-substituted compound is similar to those recently determined for the *tert*-butyl and phenyl homologues [8]. The average Ni—P bond lengths are 2.18, 2.17 and 2.15 Å for *R* = Mes, *t*Bu and Ph, respectively. In the same order, the average Ni—P—Ni angles are 98.9, 96.9 and 98.2°; the average P—Ni—P angles are 76.4, 74.6 and 74.8°; the average C—P—C angles are 108.5, 101.3 and 106.8°; the dihedral angles between the two NiP_2 planes are 35.9, 48.0 and 43.6°. The comparatively small dihedral angle of 35.9° is likely due to steric repulsion between the bulky mesityl groups and the cyclopentadienyl rings. Apart from that, the values determined for *R* = Mes and *R* = Ph are very similar.

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