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The η^2 Complex of Nickel Bis(diphenylphosphanyl)propane with Fullerene: {Ni(dppp)(η^2-C_{60})}·(Solvent) Obtained by Reduction

Dmitri V. Konarev,*[a] Salavat S. Khasanov,[b] Evgeniya I. Yudanova,[a] and Rimma N. Lyubovskaya[a]

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The η^2 complex of nickel bis(diphenylphosphanyl)propane with fullerene, {Ni(dppp)(η^2-C_{60})}·$(C_6H_{14})_{0.84}$·$(C_6H_4Cl_2)_{0.16}$ (**1**) (C_6H_{14}: hexane, $C_6H_4Cl_2$: *o*-dichlorobenzene), has been obtained by reduction of the Ni(dppp)Cl_2 and C_{60} mixture with sodium fluorenone in *o*-dichlorobenzene and slow precipitation of the single crystals by diffusion of hexane. Nickel coordinates to the 6–6 bond of C_{60} by η^2-coordination to form Ni–C(C_{60}) bonds with a length of 1.948–1.951(2) Å, which are the shortest M–C bonds among known η^2 complexes of fullerenes. The 6–6 bond length [1.488(3) Å] where the Ni atom is coordinated is noticeably longer than the average length of other 6–6 bonds in C_{60} [1.388(2) Å]. Coordination of nickel to C_{60} results in the splitting of two bands for two IR-active modes of C_{60} into three bands, because of the lower symmetry of C_{60}, and a noticeable shift in the $F_{1u}(4)$ mode of C_{60} to lower frequencies, as a result of π back-donation. The dark green complex manifests two absorption bands at 664 and 890 nm in the visible range. The complex is EPR silent since only a weak narrow signal with $g = 2.0000$ and $\Delta H = 0.17$ mT was found in the EPR spectrum of **1** at room temperature, which originates from about 0.1 % of spins of the total amount of C_{60}.

Introduction

Fullerenes form a variety of compounds such as solvates, van der Waals molecular complexes, charge-transfer complexes and salts, and transition metal complexes bonded by coordination bonds.[1–5] Some complexes show interesting magnetic, conducting, and photophysical properties.[1–5] The C_{60} molecule contains sixty identical carbon atoms. There are two different types of C–C bonds in C_{60}. A shorter 6–6 bond with a length of 1.38 Å (hexagon ring junction) behaves as an olefin unit, and different transition-metal compounds can coordinate to this bond by η^2-coordination. Fullerene coordination complexes can be prepared by using zero-valent compounds of platinum, palladium, nickel, chromium, osmium, and some other metals, $(Ph_3P)_2M$·(η^2-C_2H_4) (M = Pd, Pt), $(R_3P)_4M$ (R = Et or Ph, M = Ni, Pd, Pt), and (η^6-$C_6H_5CH_3$)$Cr(CO)_3$.[5–11] With an excess of a transition-metal compound, multiple addition to C_{60} is possible, which provides the formation of a hexa-addition product, namely, $\{(Et_3P)_2M\}_6C_{60}$, M = Pd, Pt.[12] In all cases, fullerenes substitute one or two ligands in the coordination sphere of a transition metal:

$$(Ph_3P)_2M\cdot(\eta^2\text{-}C_2H_4) + C_{60} \rightarrow (Ph_3P)_2M\cdot(\eta^2\text{-}C_{60}) + C_2H_4$$

$$(R_3P)_4M + C_{60} \rightarrow (R_3P)_2M\cdot(\eta^2\text{-}C_{60}) + 2R_3P$$

$$(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_3 + C_{60} \rightarrow (\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2\cdot(\eta^2\text{-}C_{60}) + CO \text{ (UV irradiation)}$$

Another way of preparing fullerene coordination complexes involves the addition of Vaskas-type compounds Ir-COCl$(R_3E)_2$ (E = P, As, R = alkyl or aryl) to fullerenes (C_{60}, $C_{60}O$, C_{70} and C_{84}).[13–15]

Compounds of zero-valent metals with phosphorus-containing ligands can be prepared by using a limited number of metals only. Metal cations (Ni^{2+}, Co^{2+}, Fe^{2+}, etc.) form another wide family of air-stable and synthetically available compounds.[16] In this work we developed a reduction method to prepare fullerene coordination complexes from the metal-cation-coordinated diphosphane ligand [Ni(dppp)Cl_2] and neutral C_{60}. Previously, the reduction route was used to prepare some metal–fullerene complexes and salts. For example, $(C_{60}^{\bullet-})_2\{(M^{2+})\cdot(DMF)_x\}$ salts (x = 2.4–4, M = Co, Ni, Fe, Mn, Eu, and Cd) were obtained[17] by the interaction of the $(Cs^+)(C_{60}^{\bullet-})$ salt with metal(2+) halides. Crystal structures of these salts are unknown. It was concluded from the spectroscopic data that they do not contain coordination bonds between the metals and the C_{60} anions. As a result, spins are present on both $(M^{2+})\cdot(DMF)_x$ cations and the $C_{60}^{\bullet-}$ radical anions and show fairly strong antiferromagnetic interactions.[17] PtC_{60} and PdC_{60} polymers can be obtained by the reduction of Pd^{2+} and Pd^{2+} salts in the presence of fullerenes.[18] The addition

[a] Institute of Problems of Chemical Physics RAS, Chernogolovka, Russian Federation
Fax: +7-496-522-18-52
E-mail: konarev@icp.ac.ru
[b] Institute of Solid State Physics RAS, Chernogolovka, Moscow region 142432, Russian Federation
E-mail: khasanov@issp.ac.ru
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of anionic carbonylates such as $Co(CO)_4^-$, $Mn(CO)_5^-$, $Re(CO)_5^-$, $CpFe(CO)_2^-$, $CpM(CO)_3^-$ (M = Mo, W) is realized through the reduction of C_{60} by carbonylate followed by the η^2-addition of the $M(CO)_x^{\cdot}$ radical to the fullerene anion.[19,20] Transition-metal fullerene complexes $(\mu\text{-}C_{60})Mo_2(\eta^5\text{-}C_5H_4CO_2Et)_2$ and $(\mu\text{-}C_{60})W_2(\eta^5\text{-}C_5H_4CO_2Et)_2$ were obtained through the C_{60}^{2-} dianions generated in the C_{60} reduction by potassium/1-methylnaphthalene in THF.[21]

In our work, we used sodium fluorenone as reductant, which was reported to reduce nanotubes.[22] This reductant reduces C_{60} in benzonitrile to up to the –2 charged state, C_{60}^{3-} trianions cannot be obtained even with a large excess of reductant. The reduction of a stoichiometric mixture of $Ni(dppp)Cl_2$ and C_{60} by 2.4 equiv. sodium fluorenone and dissolution of all components in *o*-dichlorobenzene results in the formation of a dark green solution. Diffusion of hexane into this solution for one month results in the precipitation of well-shaped large single crystals of $\{Ni(dppp)(\eta^2\text{-}C_{60})\}\cdot(C_6H_{14})_{0.84}\cdot(C_6H_4Cl_2)_{0.16}$ (**1**) (C_6H_{14}: hexane, $C_6H_4Cl_2$: *o*-dichlorobenzene) (Figure 1). The preparation of single crystals of **1** allows the crystal structure of the nickel–fullerene coordination complex to be determined for the first time. Though several nickel–C_{60} complexes were obtained, for example $\{(Et_3P)_2Ni\}(\eta^2\text{-}C_{60})$ and $\{(Et_3P)_2Ni\}_6(\eta^2\text{-}C_{60})$,[7,23] their crystal structures were unknown. The EPR, IR, and optical spectra of **1** were measured and discussed.

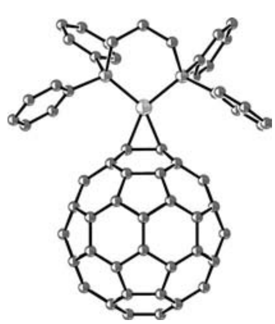

Figure 1. Molecular structure of the $Ni(dppp)(\eta^2\text{-}C_{60})$ unit. Only one major occupied orientation is shown for two of four phenyl substituents in Ni(dppp).

The crystal structure of **1** was determined at 120(2) K.[24] Two of four phenyl substituents in Ni(dppp) are disordered between two orientations with occupancies of 0.782(5)/0.218(5). There are two positions for the solvent molecules. One position is occupied by hexane and the other is shared by disordered hexane and *o*-dichlorobenzene with occupancies of 0.67/0.33. Therefore, the $C_6H_{14}/C_6H_4Cl_2$ ratio in **1** is 0.84:0.16.

Ni(dppp) coordinates to the 6–6 bond of C_{60} by η^2-coordination to form Ni–C(C_{60}) bonds with a length of 1.948–1.951(2) Å, which are the shortest M–C bonds among known η^2 complexes of fullerenes. Analysis of the CCDC data show that the lengths of the M–C bonds in the η^2 complexes of fullerenes lie in the following ranges: 2.06–2.14 Å for Pd, 2.07–2.14 Å for Pt, 2.08–2.11 Å for Mn, 2.08–2.16 Å for Rh, 2.15–2.23 Å for Ir, 2.19–2.27 Å for Os, 2.20 Å for Cr, 2.24–2.34 Å for W, and 2.28–2.37 Å for Mo. The Ni–P(dppp) distances are noticeably longer [2.152(5) and 2.158(5) Å] than the Ni–C(C_{60}) distances. The PNiP and CNiC angles are 100.67(2)° and 44.87(2)°, respectively. The 6–6 bond length of 1.488(3) Å where the Ni atom is coordinated is noticeably longer than the average length of the other 6–6 bonds in C_{60} [1.388(2) Å]. Such a bond elongation can be a result of the metal-to-C_{60} π back-donation.[7] The Ni coordination geometry is nearly planar, since the five atoms (nickel, two carbon and two phosphorus atoms bonded to nickel) are nearly coplanar with a deviation of 0.076 Å from the least-squares plane. The formation of a short Ni–C(C_{60}) coordination bond was predicted theoretically for $(PH_3)_2Ni(\eta^2\text{-}C_{60})$ units (1.989 Å).[25] Other calculated geometric parameters also have similar values (the Ni–P distance is 2.222 Å, the PNiP angle is 113° and the length of the 6–6 bond in C_{60} is 1.470 Å).[25]

The structure of the compound is layered (Figure 2). Fullerene layers are separated by bulky Ni(dppp) fragments. Each C_{60} has three neighbors in such layers. Two neighbors are located along the lattice *c* axis with a uniform center-

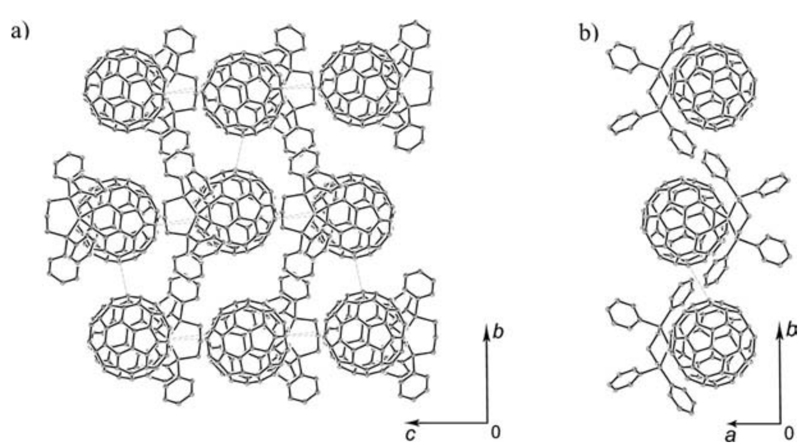

Figure 2. Packing of the coordination $Ni(dppp)(\eta^2\text{-}C_{60})$ units in **1**. View (a) along the lattice *a* axis on the fullerene layers and (b) along the lattice *c* axis and fullerene layers. Dashed lines show the shortened van der Waals C···C contacts between the fullerenes.

to-center distance of 10.033 Å. Several shortened van der Waals C···C contacts in the range 3.18–3.34 Å are formed in this direction. The third neighbor is located approximately in the *b* direction with a longer center-to-center distance of 10.217 Å and three van der Waals interfullerene C···C contacts of about 3.39 Å.

The IR spectrum of **1** shows absorption bands assigned to four F_{1u}(1–4) modes of C_{60} together with the absorption bands attributed to Ni(dppp) and solvent molecules (Supporting Information). The F_{1u}(1) and F_{1u}(3) modes are manifested as single absorption bands at 526 and 1182 cm^{-1}, respectively. Threefold degenerated F_{1u}(2) and F_{1u}(4) modes are split into three bands at 573, 577, 584 and 1412, 1416, 1419 cm^{-1}, respectively (Figure 3). Such a splitting can be due to the lower C_{60} symmetry on nickel coordination. Symmetry lowering also results in the appearance of new weak IR bands.[26] However, since Ni(dppp) shows many absorption bands in the IR spectrum, it is impossible to analyze the appearance of new weak C_{60} bands in the spectrum of **1**. The F_{1u}(4) mode of C_{60} is sensitive to charge transfer to the C_{60} molecule and its band shifts from 1429 cm^{-1} in the neutral state to 1396–1388 cm^{-1} in the radical anion state.[27–29] In the spectrum of **1**, the absorption band of this mode is noticeably shifted to lower frequencies (average position at 1416 cm^{-1}, Figure 3) relative to that of neutral C_{60}. Coordination of a transition-metal fragment on C_{60} can be accompanied by the donation from the filled π orbital of C_{60} to a vacant orbital of the metal (σ donation) and simultaneous back-donation from the occupied metal d orbital to a vacant π* orbital of C_{60} (π back-donation).[7] The observed shift can be due to π back-donation. Previously, similar effects were found in a series of $(PR_3)_2M(\eta^2\text{-}C_{60})$ complexes (M = Ni, Pd, Pt) studied by Raman spectroscopy.[30] Similarly to the IR spectra, coordination of a transition-metal fragment to C_{60} splits the bands of some degenerated Raman active modes as a result of lower C_{60} symmetry and shifts the high-frequency C_{60} modes to lower frequencies as a result of π back-donation.[30] Symmetry-lowering effects were observed in the IR spectra of σ-bonded coordination cobalt(II) tetraphenylporphyrin–fullerene {Co^{II}porphyrin(C_{60}^-)} anions[4,31] and in the Raman spectra of some η^2-coordination complexes: $[M(PEt_3)_2]_6C_{60}$[30] and $IrCO(\eta^5\text{-}C_9H_7)(\eta^2\text{-}C_{60})$.[32] The increase in electron density on C_{60} from π back-donation in the $(PR_3)_2M(\eta^2\text{-}C_{60})$ complexes (M = Ni, Pd, Pt) is also justified by electrochemical investigation since all three reductions waves for the fullerenes in these complexes are shifted by 0.32–0.34 V to the cathode region relative to those of C_{60}.[23,33]

The solution of complex **1** is dark green. The spectrum of **1** was measured in *o*-dichlorobenzene under anaerobic conditions (Figure 4) and shows three bands in the visible range. The band at 610 nm can be attributed to symmetry-forbidden transitions in fullerene. The increase in intensities of these transitions can be due to symmetry breaking of C_{60} as a result of the addition of Ni(dppp). Two bands at 436 and 672 nm are typical for fullerene addition products. The latter band is observed in the spectra of different η^2 complexes of C_{60} and can be attributed to intramolecular charge transfer in the coordination metal–C_{60} units.[5,11,34] Similar solution spectra were observed for other transition-metal complexes of C_{60}. For example, $(\eta^6\text{-}C_6H_5CH_3)Cr(CO)_2(\eta^2\text{-}C_{60})$ shows three bands in the visible range of its spectra at 448, 602 and 650 nm,[10] whereas the addition product of $H_3Ir(PPh_3)_3$ to C_{60} showed bands at 435, 602 and 650 nm.[35] The spectrum of **1** was also measured in a KBr pellet (Figure 4, inset). It also shows an intense band at 664 nm observed in the solution spectrum and a weaker broad band at 890 nm (Figure 4, inset). Since this band is absent in the solution spectrum, it can be assigned to intermolecular charge transfer between closely packed Ni(dppp)(η^2-C_{60}) units.

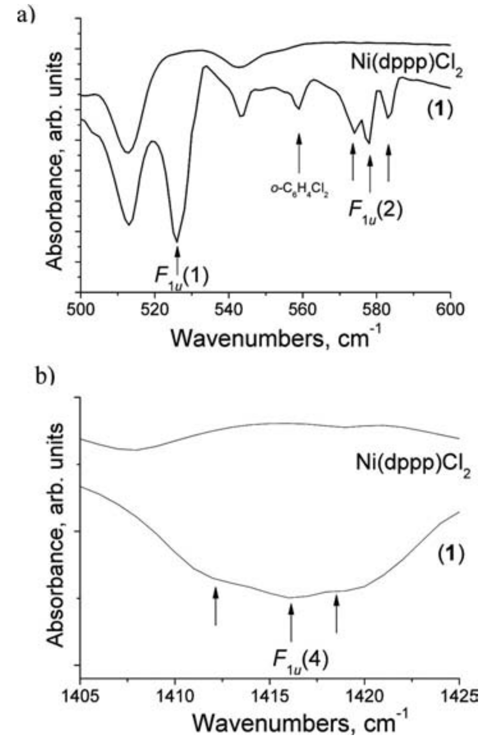

Figure 3. IR spectrum of starting $Ni(dppp)Cl_2$ and complex (**1**) in a KBr pellet. Absorption bands attributed to the F_{1u}(1), F_{1u}(2) and F_{1u}(4) modes of C_{60} are shown by arrows.

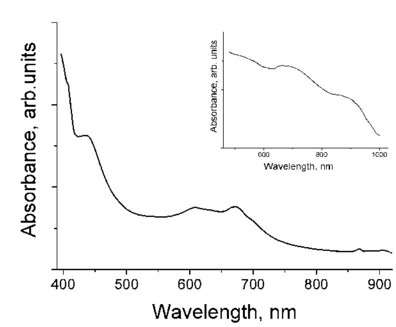

Figure 4. The spectrum of complex **1** in *o*-dichlorobenzene solution in the range 400–920 nm. The inset shows the spectrum of **1** in a KBr pellet in the range 480–1000 nm.

In the EPR spectrum of **1** (measured under anaerobic conditions), only a weak narrow signal with $g = 2.0000$ and $\Delta H = 0.17$ mT is observed at room temperature. The integral intensity of this signal corresponds to the contribution of about 0.1% of spins from the total amount of C_{60}. Therefore, complex **1** is EPR silent and does not contain unpaired spins.

Thus, in this work we used the reduction method to prepare a transition-metal fullerene complex from a diphosphane compound, $[Ni(dppp)Cl_2]$, and neutral C_{60}: $\{Ni(dppp)(\eta^2\text{-}C_{60})\}\cdot(C_6H_{14})_{0.84}\cdot(C_6H_4Cl_2)_{0.16}$ (**1**). The preparation and investigation of similar complexes with other metals are in progress. Complex **1** was obtained as single crystals, which allows the determination of the crystal structure of the coordination nickel–fullerene complex for the first time. Coordination of nickel leads to unusually short Ni–C(C_{60}) bonds with lengths of 1.948–1.951(2) Å, which are the shortest among known fullerene η^2 complexes. Coordination results in a lower C_{60} symmetry and a slight shift in the $F_{1u}(4)$ C_{60} mode to lower frequencies because of π back-donation. In spite of this shift, **1** can be considered as a complex between zero-valent nickel and neutral C_{60} since the position of $F_{1u}(4)$ C_{60} mode is closer to the neutral state than to the radical anion state of fullerene. Magnetic measurements indicate that **1** is EPR silent. Complex **1** demonstrates strong absorption in the visible range. It has a layered structure and can be expected to show interesting photophysical properties. Previously, it was shown that layered fullerene complexes can possess high photoconductivity[36,37] and manifest photoinduced charge separation.[38]

Experimental Section

Materials: $Ni(dppp)Cl_2$ was purchased from Aldrich. C_{60} of 99.98% purity was received from MTR Ltd. Solvents were purified in argon. *o*-Dichlorobenzene ($C_6H_4Cl_2$) was distilled from CaH_2 under reduced pressure, and benzene and hexane were distilled from Na/benzophenone. The solvents were degassed and stored in a glove box. All manipulations for the synthesis of **1** were carried out in a MBraun 150B-G glove box with controlled atmosphere and a content of H_2O and O_2 less than 1 ppm. The crystals were stored in a glove box and loaded under anaerobic conditions in 5-mm quartz tubes for EPR measurements. The KBr pellet for IR was prepared in the glove box.

Synthesis: Sodium fluorenone was obtained by the reduction of fluorenone (2 g, 0.011 mol) with metallic sodium (230 mg, 0.01 mol) in benzene (30 mL) at 60 °C with intense stirring over 24 h under anaerobic conditions. Sodium completely dissolved, and a brown precipitate of extremely air-sensitive sodium fluorenone was formed. It was filtered, washed with two portions (5 mL) of hexane, dried, and stored in the glove box.

Crystals of **1** were obtained by the reduction of a stoichiometric mixture of $Ni(dppp)Cl_2$ (22.6 mg, 0.042 mmol) and C_{60} (30 mg, 0.042 mmol) in *o*-dichlorobenzene (10 mL) by sodium fluorenone (20 mg, 0.098 mmol, 2.4 equiv.). After several minutes, all components were dissolved to yield a clear dark green solution. $Ni(dppp)(\eta^2\text{-}C_{60})\cdot(C_6H_{14})_{0.84}\cdot(C_6H_4Cl_2)_{0.16}$ (**1**) precipitated over one month as well-shaped large black parallelepipeds by diffusion of hexane, which was layered over the *o*-dichlorobenzene solution. The solvent was decanted from the crystals, which were washed with hexane. Crystals with a size of up to $1\times 1\times 0.5$ mm were obtained in 52% yield.

General: FTIR spectra were measured in KBr pellets with a Perkin–Elmer 1000 Series spectrometer (400–7800 cm^{-1}). The UV/Vis spectrum was measured in a KBr pellet on a Shimadzu-3100 spectrometer in the range 400–1000 nm. The EPR spectrum of **1** was recorded at room temperature with a Radiopan SE/X-2547 spectrometer. For the estimation of the number of spins in **1**, the integral intensity of the signal from a weighed amount of the complex was compared to that of the signal from a sample of α,α′-diphenyl-β-picrylhydrazid (DPPH) with a known amount of spins.

X-ray Crystallographic Study: X-ray diffraction data for **1**[24] were collected at 120(2) K on an Oxford diffraction "Gemini-R" CCD diffractometer with graphite monochromated Mo-K_α radiation with an Oxford Instrument Cryojet system. Raw data reduction to F^2 was carried out by using CrysAlisPro, Oxford Diffraction Ltd. The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2 by using SHELX-97.[39] Non-hydrogen atoms were refined in the anisotropic approximation. Positions of the hydrogen atoms were calculated geometrically. Subsequently, the positions of the H atoms were refined by the "riding" model with $U_{iso} = 1.2U_{eq}$ of the connected non-hydrogen atom or as ideal CH_3 groups with $U_{iso} = 1.5U_{eq}$.

Supporting Information (see footnote on the first page of this article): IR data and spectra of the starting compounds and of **1** are presented.

Acknowledgments

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[1] B. Gotschy, *Fullerene Sci. and Technol.* **1996**, *4*, 677–698.
[2] D. V. Konarev, R. N. Lyubovskaya, *Russ. Chem. Rev.* **1999**, *68*, 19–38.
[3] D. M. Guldi, *Chem. Soc. Rev.* **2002**, *31*, 22–36.
[4] D. V. Konarev, S. S. Khasanov, R. N. Lyubovskaya, *Russ. Chem. Bull.* **2007**, *56*, 371–392.
[5] A. L. Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123–2165.
[6] P. J. Fagan, J. C. Calabrese, B. Malone, *Science* **1991**, *252*, 1160–1161.
[7] P. J. Fagan, J. C. Calabrese, B. Malone, *Acc. Chem. Res.* **1992**, *25*, 134–142.
[8] V. V. Bashilov, P. V. Petrovskii, V. I. Sokolov, S. V. Lindeman, I. A. Guzey, Yu. T. Struchkov, *Organometallics* **1993**, *12*, 991–992.
[9] L.-C. Song, G.-A. Yu, Q.-M. Hu, C.-M. Che, N. Zhu, J.-S. Huang, *J. Organomet. Chem.* **2006**, *691*, 787.
[10] Yu. A. Shevelev, G. V. Markin, D. V. Konarev, G. K. Fukin, M. A. Lopatin, A. S. Shavyrin, E. V. Baranov, R. N. Lyubovskaya, G. A. Domrachev, *Dokl. Chem.* **2007**, *412*, 18–21.
[11] A. V. Usatov, E. V. Martynova, I. S. Neretin, Y. L. Slovokhotov, A. S. Peregudov, Y. N. Novikov, *Eur. J. Inorg. Chem.* **2003**, 2041–2044.
[12] P. J. Fagan, J. C. Calabrese, B. Malone, *J. Am. Chem. Soc.* **1991**, *113*, 9408–9409.
[13] A. L. Balch, V. J. Catalano, J. W. Lee, *Inorg. Chem.* **1991**, *30*, 3980–3981.
[14] A. L. Balch, V. J. Catalano, J. W. Lee, M. M. Olmstead, S. R. Parkin, *J. Am. Chem. Soc.* **1991**, *113*, 8953–8955.
[15] A. L. Balch, A. S. Ginwalla, J. W. Lee, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1994**, *116*, 2227–2228.
[16] W. Levason, "Phosphane Complexes of Transition Metals" in *The Chemistry of Organophosphorus Compounds*, F. R. Hartley (Ed.), Wiley, **1990**, Vol. 1, pp. 568–641.

[17] D. V. Konarev, R. N. Lyubovskaya, *Russ. Chem. Bull.* **2008**, *57*, 1944–1954.

[18] A. L. Balch, D. A. Costa, K. Winkler, *J. Am. Chem. Soc.* **1998**, *120*, 9614–9620.

[19] M. Bengough, D. M. Thompson, M. C. Baird, G. D. Enright, *Organometallics* **1999**, *18*, 2950–2952.

[20] D. M. Thompson, J. H. Brownie, M. C. Baird, *Full. Nanot. Carb. Nanostr.* **2004**, *12*, 697–713.

[21] Y.-H. Zhu, L.-C. Song, Q.-M. Hu, C. M. Li, *Org. Lett.* **1999**, *1*, 1693–1695.

[22] P. Petit, C. Mattis, C. Journet, P. Bernier, *Chem. Phys. Lett.* **1999**, *305*, 370–374.

[23] S. A. Lerke, B. A. Parkinson, D. H. Evans, P. J. Fagan, *J. Am. Chem. Soc.* **1992**, *114*, 7807–7813.

[24] Crystallographic data for **1**: $C_{186}H_{76.70}Cl_{0.66}Ni_2P_4$, M_r = 2575.83 g mol^{-1}, black, monoclinic, $P2_1/c$, a = 13.6452(5), b = 21.0574(7), c = 20.0333(7) Å, β = 102.707(4)°, V = 5615.2(4) Å^3, Z = 2, $d_{calcd.}$ = 1.523 g cm^{-3}, μ = 0.478 mm^{-1}, T = 120(2) K, max. 2θ = 57.4°, R_{int} = 0.0289, reflections $I > 2\sigma(I)$ = 12278, R_1 = 0.0531 [$I > 2\sigma(I)$], wR_2 = 0.1513, data/parameters 104/871, G.O.F. = 1.045. CCDC-795553 contains 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.

[25] F. Nunzi, A. Sgamellotti, N. Re, C. Floriani, *Organometallics* **2000**, *19*, 1628–1634.

[26] D. V. Konarev, R. N. Lyubovskaya, N. V. Drichko, E. I. Yudanova, Y. M. Shul′ga, A. L. Litvinov, V. N. Semkin, B. P. Tarasov, *J. Mater. Chem.* **2000**, *10*, 803–818.

[27] T. Picher, R. Winkler, H. Kuzmany, *Phys. Rev. B* **1994**, *49*, 15879–15889.

[28] N. V. Semkin, N. G. Spitsina, S. Krol, A. Graja, *Chem. Phys. Lett.* **1996**, *256*, 616–622.

[29] D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, Y. Yoshida, R. N. Lyubovskaya, *J. Am. Chem. Soc.* **2003**, *125*, 10074–10083.

[30] B. Chase, P. J. Fagan, *J. Am. Chem. Soc.* **1992**, *114*, 2252–2256.

[31] D. V. Konarev, S. S. Khasanov, A. Otsuka, Y. Yoshida, R. N. Lyubovskaya, G. Saito, *Chem. Eur. J.* **2003**, *9*, 3837–3848.

[32] Y. Zhang, Y. Du, J. R. Shapley, M. J. Weaver, *Chem. Phys. Lett.* **1993**, *205*, 508–514.

[33] S. A. Lerke, D. H. Evans, P. J. Fagan, *J. Electroanal. Chem.* **1995**, *383*, 127–132.

[34] N. N. Denisov, A. S. Lobach, V. A. Nadtochenko, *Russ. Chem. Bull.* **1996**, *45*, 1103–1106.

[35] N. F. Goldshleger, N. N. Denisov, V. A. Nadtochenko, M. G. Kaplunov, A. V. Kulicov, *Russ. Chem. Bull.* **1997**, *46*, 2032–2035.

[36] D. V. Konarev, D. V. Lopatin, V. V. Rodaev, A. V. Umrikhin, S. S. Khasanov, G. Saito, K. Nakasuji, A. L. Litvinov, R. N. Lyubovskaya, *J. Phys. Chem. Solids* **2005**, *66*, 711–715.

[37] D. V. Lopatin, V. V. Rodaev, A. V. Umrikhin, D. V. Konarev, A. L. Litvinov, R. N. Lyubovskaya, *J. Mater. Chem.* **2005**, *15*, 657–660.

[38] D. V. Konarev, G. Zerza, M. C. Scharber, N. S. Sariciftci, R. N. Lyubovskaya, *Mol. Cryst. Liq. Cryst.* **2005**, *427*, 315–333.

[39] G. M. Sheldrick, *SHELX97*, University of Göttingen, Germany, **1997**.

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