

Novel tetrahedral tetranickel cluster with alkyldiyne ligand (NiCp)₄(μ₃-CR)

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Abstract

A novel tetrahedral (μ₃-alkyldiyne)tetranickel cluster (NiCp)₄(μ₃-C(CH₂)₄CH₃) (**4**) was obtained in the reaction of nickelocene with potassium and 1-hexene. Compound **4** was characterised by means of MS and X-ray diffraction analysis. It crystallizes in the orthorhombic crystal system and *Pna*2₁ (No. 33) space group. Unit cell dimensions: *a* = 28.406(6) Å, *b* = 8.928(2) Å, *c* = 9.541(2) Å; *Z* = 4. The compound possesses 63 valence electrons, three more than the expected “magic number” for such type of clusters, and three of the four nickel atoms do not fulfil the 18VE rule. It is paramagnetic with the magnetic moment 3.54 μ_B, what corresponds to three unpaired electrons per molecule. This was confirmed by molecular orbital calculations using the density functional theory (DFT).

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1. Introduction

Tetrakis(η⁵-cyclopentadienyl)nickel cluster (NiCp)₄ has not been obtained so far, although it possesses the magic number of electrons (60) and all nickel atoms fulfil the 18 valence electron rule. Clusters of the type (NiCp)₄H_{*n*} (*n* = 3 [1], *n* = 2 [2]) were synthesised, and neutron diffraction analysis [1b] showed that hydride ligands are located on three faces of the Ni₄ tetrahedral core. (NiCp)₄H₃ cluster has additional, unpaired electrons making it paramagnetic. On the other hand, (NiCp)₄H₂ cluster is diamagnetic. Although both clusters do not fulfil 18 valence electron rule (they possess 63 and 62 electrons, respectively) they are apparently stable.

(μ₃-Alkyldiyne)tetranickel cluster has not been reported so far, in contrary to (μ₃-alkyldiyne)trinickel clusters, which were obtained by various methods and fully characterised [3].

Other transition metals clusters of the type (μ₃-alkyldiyne)M₄L_{*n*} are known and well documented in the literature [4]. All these clusters, regardless of ligands, possess the “magic number” of valence electrons and metal atoms fulfil 18 valence electron rule. There are only two examples of organometallic tetrahedral tetranickel clusters with ligands other than Cp [5]. In both of them the number of valence electrons fulfils 18 valence electron rule.

Hexanickel cluster (NiCp)₆ was also synthesised [6]. In fact it has 90 valence electrons (4 more than “magic number”) and all nickel atoms do not fulfil 18 valence electron rule.

In this paper, we report the synthesis and characterisation of the first (μ₃-alkyldiyne)tetranickel cluster.

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2. Results and discussion

We have reported [7] that nickelocene reacts with sodium and terminal alkenes in THF, forming several products, among which (μ_3 -alkylidyne)trinickel cluster and its hydride were present. In these reactions tetranickel cluster was not formed.

Changing the reducing agent from sodium to potassium enabled us to get a novel (μ_3 -alkylidyne)tetranickel cluster. When the reaction was carried out in THF solution, nickelocene was reduced to the metallic nickel which coated pieces of potassium and stopped the reaction, so we were forced to use toluene as a solvent.

The reaction between nickelocene, potassium and 1-hexene (molar ratio 1:1.4:2) was carried in toluene at room temperature for 72 h. The residue was then filtered through the bed of alumina, to separate nickel clusters from KCp formed in the reaction, and concentrated. A mixture of nickel clusters was chromatographed on neutral alumina using hexane and hexane/toluene as eluents. Five main fractions were collected (Scheme 1):

The first green fraction contained small amount of unreacted nickelocene.

The second fraction contained compound **1** and traces of **2**. The third fraction contained the cluster **3** and the fifth contained the cluster **5**. All these compounds were described earlier [7].

The fourth green fraction contained paramagnetic solid (NiCp)₄(μ_3 -CCH₂CH₂CH₂CH₂CH₃) (**4**) (yield ~10%). After crystallisation from hexane, dark crystals appropriate for X-ray measurements were obtained. These crystals were well soluble in organic solvents (hexane, alcohols, toluene, THF, etc.). In a solid state, compound **4** reacted slowly with oxygen, whereas its solutions oxidized easily. The compound was stable towards water.

Cluster **4** decomposes slowly during chromatography. Two brown bands emerge from the green band formed by **4**. They were identified as trinickel cluster **3** and tetranickel cluster **5**. It is much better to isolate pure compound **4** during the first chromatography (even losing quite a lot of it), and do not try to purify it by the second chromatography, because it may decompose completely.

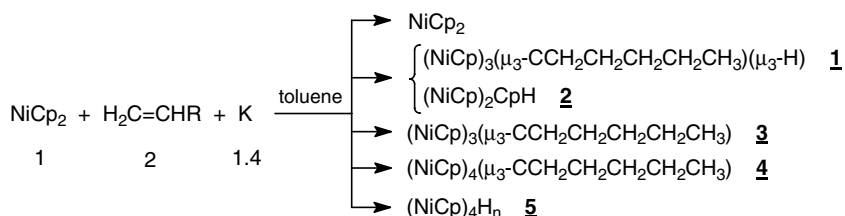
MS spectrum of **4** revealed the parent ion at *m/e* 575 (⁵⁸Ni calc.) with an isotopic pattern characteristic for four nickel atoms in a molecule. There were no signals in ¹H NMR spectrum of **4**, at the range between 0 and 10 ppm, what suggested that the compound was paramagnetic.

However, there were no signals in X-band EPR spectrum at room temperature and at 77 K in a solid state as well as in a benzene solution. Magnetic susceptibility was determined by NMR measurements at 298 K by Evans method [8,9] from differences in chemical shifts of methyl group protons of toluene used as a solvent and as an external standard. The magnetic moment calculated from these measurements was 3.54 μ_B , what confirmed paramagnetism of the compound **4** and corresponded to three unpaired electrons per molecule.

These observations were confirmed by molecular orbital calculations using the density functional theory (DFT). The energies of doublet and quartet states were calculated at UB3LYP/6-31G* for both the X-ray structure and the UB3LYP/3-21G* optimized gas phase geometry. Calculations predict that the quartet state in both cases is significantly more stable. The corresponding quartet–doublet energy differences are 8.9 and 8.6 kcal/mol for the X-ray structure and for the calculated geometry, respectively.

Although the applied level of theory does not secure high accuracy, we believe that it allows a qualitative insight into the electronic structure of the cluster **4**. Open-shell energy calculations for the transition metal clusters may be tricky. However, the accurate calculations for the system under question would be significantly more expensive, while it is not the main point of this study. Qualitative significance of these calculations is supported by the fact that the geometry of cluster **4** optimized at the relatively low level of theory is in reasonable agreement with the X-ray structure. The calculated and measured bond lengths and angles are very similar, except for the distances of the axial Ni atom from equatorial ones, which in the optimized geometry are by ca. 0.16 Å shorter than in the X-ray structure (Fig. 1).

The Ni₄C skeleton has geometry of slightly deformed trigonal bipyramid, with carbon atom in one of the axial positions. Its symmetry is close to C_{3v}, as the distances between equatorial nickel atoms (Ni(1), Ni(2) and Ni(3)) and axial atoms (C(1) and Ni(4)) are not equal (Fig. 1). This asymmetry is probably due to the arrangement of the alkyl chain. The Ni–Cp distances are not equal, too. The agreement between Ni–C distances measured by X-ray (2.06–2.16 Å) and calculated for the quartet **4** (2.06–2.14 Å) is very good. For the doublet **4** they are slightly longer (2.07–2.17 Å) which suggests somewhat weaker Ni–Cp interactions in this electronic state. The Ni–Cp distances in **4** are significantly shorter than in triplet nickelo-



Scheme 1. Compounds separated by column chromatography on alumina.

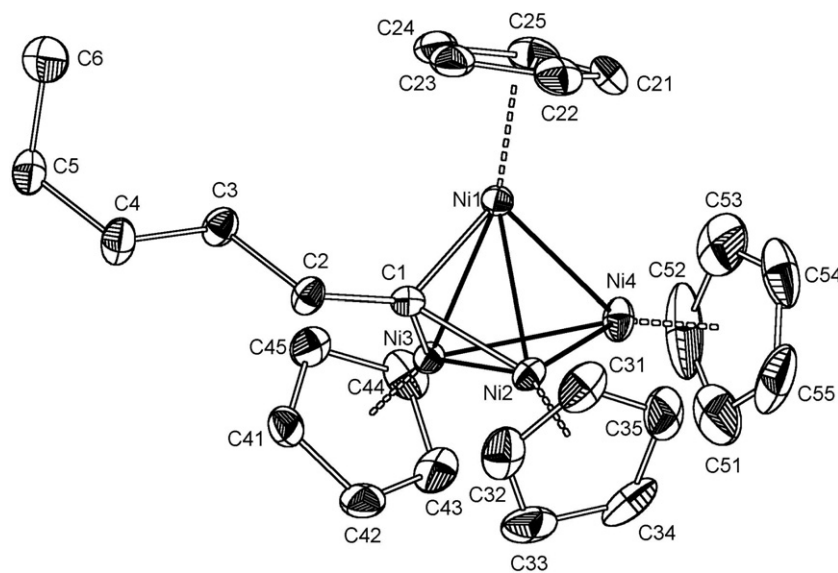


Fig. 1. The ORTEP drawing of **4** with atom numbering scheme. The thermal displacement ellipsoids are drawn at the 20% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths and angles (\AA , $^\circ$, B3LYP/3-21G* calculated values in square brackets): Ni(1)–Ni(2) = 2.423(1) [2.402], Ni(1)–Ni(3) = 2.459(1) [2.411], Ni(2)–Ni(3) = 2.408(1) [2.404], Ni(1)–Ni(4) = 2.460(1) [2.302], Ni(2)–Ni(4) = 2.465(1) [2.295], Ni(3)–Ni(4) = 2.463(1) [2.298], Ni(1)–C(1) = 1.800(6) [1.790], Ni(2)–C(1) = 1.844(6) [1.791], Ni(3)–C(1) = 1.822(6) [1.789]; Ni(1)–C(1)–Ni(2) = 83.32(24) [84.25], Ni(1)–C(1)–Ni(3) = 85.51(24) [84.69], Ni(2)–C(1)–Ni(3) = 82.12(23) [84.35], Ni(1)–Ni(4)–Ni(2) = 58.93(3) [62.99], Ni(1)–Ni(4)–Ni(3) = 59.95(3) [63.21], Ni(2)–Ni(4)–Ni(3) = 58.51(3) [63.11].

cene (ca. 2.20 \AA) [10] indicating that the Ni–Cp interactions in cluster **4** are significantly stronger.

Natural bond orbital analysis shows that the unpaired electrons are highly delocalized onto the cyclopentadienyl rings. This delocalization involves d and 4s electrons of Ni and the σ_{CC}^* orbitals of cyclopentadiene. The natural charge analysis shows almost equal charge population on all four nickel atoms ($q_{Ni} = +0.84 e$) and on all cyclopentadienyl ligands (overall charge $q_{Cp} = -0.65 e$). The charge in the cyclopentadienyl ligands is evenly distributed over all carbon and hydrogen atoms. This delocalization may partially account for the relative stability of the quartet electron configuration.

Crystals of **4** suitable for X-ray diffraction studies were obtained from hexane solution. The molecular structure of **4** is presented in Fig. 1. Crystal data, data collection and refinement parameters are given in Table 1.

The compound crystallises in the orthorhombic crystal system. The core of the cluster consists of four nickel atoms which form slightly distorted tetrahedron. Alkylidyne carbon atom is placed over one face of this tetrahedron and bonded to three nickel atoms (Ni(1), Ni(2) and Ni(3); see Fig. 1). The average bond length between three nickel atoms and alkylidyne carbon atom is 1.82 \AA , which is comparable to corresponding values measured for alkylidyne trinickel clusters [3c,7]. The average bond length between all nickel atoms is 2.45 \AA . This distance is shorter by 0.02 \AA than corresponding value in $(NiCp)_4H_3$ [1], but longer by 0.06 \AA than in $(NiCp)_4H_2$ [2].

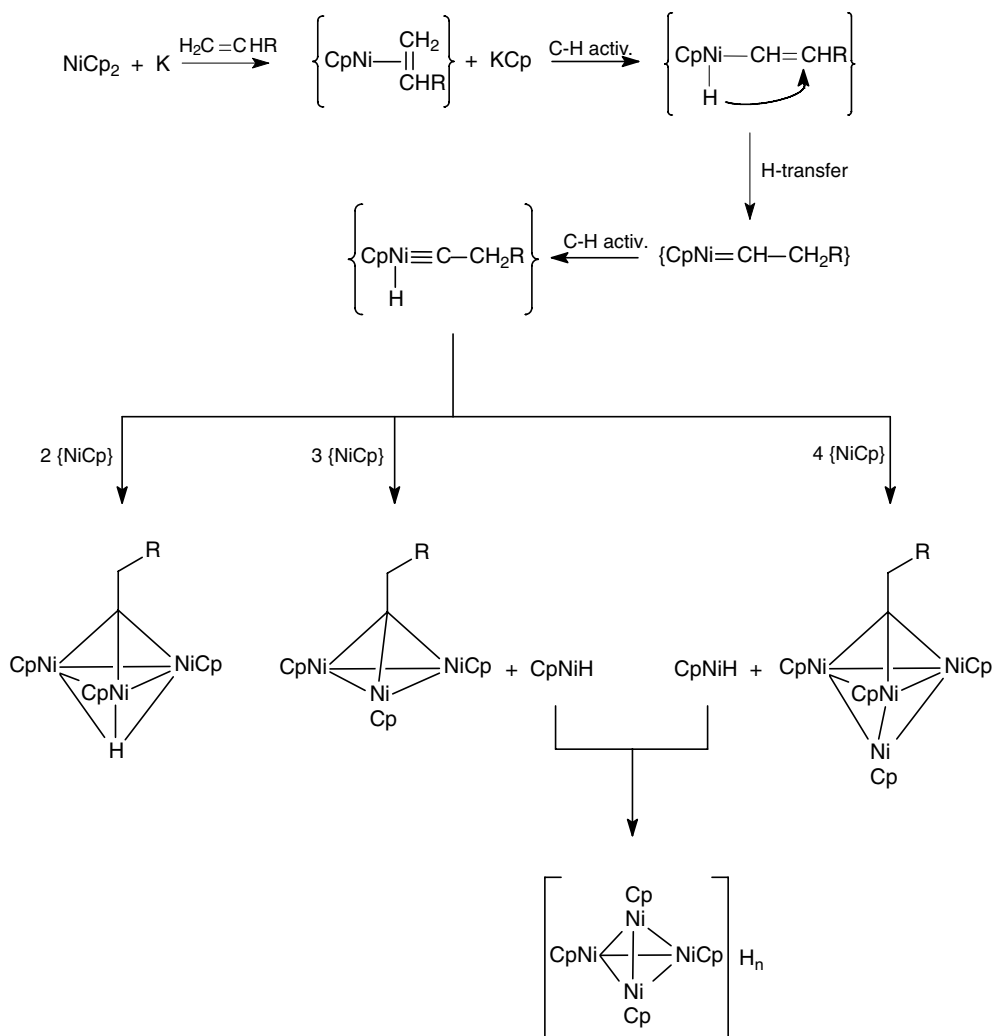
The compound **4** is the first tetranuclear cyclopentadienylnickel cluster with μ_3 -alkylidyne ligand. Although it possesses 63 valence electrons it is quite stable in an inert

atmosphere. The stability of this and other cyclopentadienyltetranickel clusters $(NiCp)_4H_3$ [1] and $(NiCp)_4H_2$ [2] is an interesting feature. On the other hand, synthesis of tetrakis(η^5 -cyclopentadienyl)tetranickel cluster which would

Table 1
Crystal data and structure refinement parameters for **4**

Empirical formula	$C_{26}H_{31}Ni_4$
Formula weight	578.35
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	Orthorhombic
Space group	$Pna2_1$ (No. 33)
<i>Unit cell dimensions</i>	
<i>a</i> (\AA)	28.406(6)
<i>b</i> (\AA)	8.928(2)
<i>c</i> (\AA)	9.541(2)
<i>V</i> (\AA^3)	2419.7(9)
<i>Z</i>	4
D_{calc} (Mg/m^3)	1.588
Absorption coefficient (mm^{-1})	3.075
Maximum and minimum transmission	1.000 and 0.715
<i>F</i> (000)	1196
Crystal size (mm)	0.35 \times 0.42 \times 0.56
θ Range for data collection ($^\circ$)	3.12–27.49
Limiting indices	$-36 \leq h \leq 36$; $0 \leq k \leq 11$; $0 \leq l \leq 12$
Number of reflections collected/unique	2868/2507 ($R_{int} = 0.0252$) $R(\sigma) = 0.0339$
Number of data/restraints/parameters	2868/1/272
Goodness of fit on F^2	1.076
Final <i>R</i> indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0392$; $wR_2 = 0.1008$
<i>R</i> indices (all data)	$R_1 = 0.0482$; $wR_2 = 0.0986$
Largest difference in peak and hole ($e \text{\AA}^{-3}$)	0.547 and -0.458

^a $R_1 = \sum(F_o - F_c)/\sum F_o$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0622P)^2 + 0.2690P$, where $P = (F_o^2 + 2F_c^2)/3$.



Scheme 2. The proposed course of the reaction.

have possessed the magic number of valence electrons (60) has been unsuccessful so far. These facts prove that the most probably tetranickel compounds, in which nickel atoms are bonded to cyclopentadienyl ligands, are stable only when they have more than 60 valence electrons. The needed extra electrons are donated by alkyldyne or hydride ligands.

The proposed course of the reaction, and the way of the formation of tri- and tetranickel clusters are shown in Scheme 2. Nickelocene reacts with potassium to give an unstable species $\{\text{NiCp}\}$ [7,11] which forms a π -complex with alkene. C–H bond activation results in formation of $\{\text{CpNi}(\text{H})\text{CH}=\text{CHR}\}$. This is followed by a transfer of a hydrogen to β -carbon, and repeated C–H bond activation leading to the formation of $\{\text{CpNi}(\text{H})\equiv\text{CCH}_2\text{R}\}$. This species reacts with $\{\text{NiCp}\}$ forming the final products.

3. Conclusions

The tetrahedral [1,2], square planar [12] and octahedral [6] cyclopentadienylnickel clusters, $(\text{NiCp})_n$ ($n = 4; 6$), are stable only when they possess more than so-called “magic

numbers” of valence electrons, and each nickel atom has on average more than 18 valence electrons. Clusters of the type $(\text{NiCp})_4$ may achieve this by adopting additional ligands. In the examples known up to now these ligands were hydrides [1,2] or selenium [12]. In this work we proved that alkyldyne carbon $\equiv\text{CR}$ can also act as a source of three additional electrons. In the case of hexanickel cluster addition of further ligands is not necessary, as the octahedral $(\text{NiCp})_6$ cluster possesses 90 valence electrons – 4 more than it appears from the rule described by Mingos [13]. These observations incline to an assumption that cyclopentadienyl ligands do not donate enough electrons to nickel to achieve a stable structure.

4. Experimental

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. ^1H and ^{13}C NMR spectra were measured on a Varian Mercury 400 MHz instrument. Mass spectra were recorded on an AMD-604 spectrometer. EPR spectra were measured on Bruker ESP

300 spectrometer in X-band. Magnetic susceptibility was determined by NMR measurements at 298 K according to Evans method [8,9] from differences in chemical shifts of methyl group protons of toluene used as the solvent and as the external standard. The magnetic moment was calculated from the measurements of magnetic susceptibility.

4.1. Reaction of nickelocene with potassium and 1-hexene in toluene

Nickelocene (2.41 g, 12.8 mmol), 1-hexene (3 cm³, 2.02 g, 24 mmol), potassium (0.70 g, 17.9 mmol) and 100 cm³ of toluene were placed in Schlenk flask and stirred at room temperature for 72 h. The reaction mixture was then filtered through the alumina layer, and the solvent was evaporated. The residue was dissolved (7 cm³ of hexane + 5 cm³ of toluene) and chromatographed on alumina (deactivated with 5% of water) with hexane and hexane/toluene mixture as eluents. Five coloured bands were separated and collected.

The first green fraction (hexane/toluene 20:1) after evaporation to dryness gave traces of solid identified as unreacted nickelocene.

The second deep-red fraction (hexane/toluene 4:1) after evaporation to dryness gave small amount of red solid identified as **1**. EIMS (70 eV) *m/e* (rel. int.) (⁵⁸Ni): 453 (M⁺, 54%), 383 (20%), 369 (97%), 343 (15%), 329 (30%), 303 (43%), 246 (33%), 188 (37%), 123 (27%). Traces of complex **2** were also present in this fraction.

The third brown fraction (hexane/toluene 4:1) after evaporation to dryness gave brown solid identified as **3** (yield 0.212 g, 0.47 mmol, ca. 11%). ¹H NMR (C₆D₆) δ (ppm): 5.17 (s, 15H, Cp), 3.69 (t, 2H, ≡C–CH₂–), 2.13 (m, 2H, –CH₂–), 1.55 (m, 4H, 2× –CH₂–), 1.02 (t, 3H, –CH₃); ¹³C NMR (C₆D₆) δ (ppm): 295.34 (C alkylidyne), 87.93 (Cp), 57.83 (CH₂), 35.73 (CH₂), 32.63 (CH₂), 23.22 (CH₂), 14.55 (CH₃). EIMS (70 eV) *m/e* (rel. int.) (⁵⁸Ni): 452 (M⁺, 74%), 384 (58%), 344 (54%), 330 (44%), 304 (93%), 246 (39%), 188 (32%), 123 (26%).

The fourth, deep-green fraction (hexane/toluene 3:1) after evaporation to dryness gave 0.221 g (yield ca. 12%) of green solid. Crystallisation from hexane gave crystals of **4**. Anal. Calc. for C₂₆H₃₁Ni₄: C, 54.00; H, 5.40. Found: C, 53.52; H, 5.48%. EIMS (70 eV) *m/e* (rel. int.) (⁵⁸Ni): 575 (M⁺, 25%), 467 (68%), 427 (36%), 384 (26%), 304 (50%), 246 (29%), 188 (54%), 123 (38%). The crystal structure of **4** was determined by X-ray measurements.

The fifth black fraction (hexane/toluene 3:1), after evaporation to dryness gave black solid identified as a mixture of clusters **5** (yield 0.126 g, ca. 8%).

4.2. Crystal structure determination

The crystal was sealed in a glass capillary under nitrogen stream. X-ray data were collected on a Nonius

Kappa CCD diffractometer (graphite monochromated Mo K α radiation). Diffractometer control program COLLECT [14], unit cell parameters and data reduction with Denzo and Scalepack [15], structure solved by direct methods SHELXS-97 [16] and refined on *F*² by full-matrix least-squares with SHELXL-97 [17]. All the hydrogen atoms were placed in calculated positions and refined using a riding model.

4.3. Quantum mechanical calculations

Density functional calculations were performed with the Gaussian 03 program [18]. Single point unrestricted open-shell calculations were carried out for the X-ray determined geometry of the tetranickel complex **4** assuming doublet, quartet and sextet electron configurations, using the B3LYP hybrid functional [19] and the Pople 6-31G* basis set [20]. Stability of the single-determinant wavefunction was verified by the stable=opt calculations. The quartet state appears to be the most stable. At this level of theory it is by ca. 9 and 38 kcal/mol lower in energy than the doublet and sextet states, respectively.

To confirm the results obtained for the X-ray structure, geometry optimizations were carried out at the UB3LYP/3-21G* level for **4**, assuming doublet and quartet electron configurations and the gas phase conditions. Stability of the wavefunction was confirmed by the stable=opt calculations. Gas phase optimized geometries of doublet and quartet states are very similar. The calculated bonding parameters are also similar to those found empirically, except for the the distances of the axial Ni atom from equatorial ones, which in the optimized geometry are by ca. 0.15 Å shorter than those in the crystal structure (see the Fig. 1 caption). Natural charge analysis was performed using the NBO 3.1 program built in the Gaussian 03 package [21].

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Appendix A. Supplementary material

Crystallographic data for the structural analysis of **4** have been deposited with the Cambridge Crystallographic Data Centre. CCDC 249743 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.09.042](https://doi.org/10.1016/j.jorganchem.2006.09.042).

References

- [1] (a) J. Müller, H. Dorner, G. Huttner, H. Lorenz, *Angew. Chem.* 85 (1973) 1117;
(b) T.F. Koetzle, J. Müller, D.L. Tipton, D.W. Hart, R. Bau, *J. Am. Chem. Soc.* 101 (1979) 5631.
- [2] S. Pasykiewicz, W. Buchowicz, A. Pietrzykowski, T. Głowiak, *J. Organomet. Chem.* 536 (1997) 249.
- [3] (a) T.I. Voyevodskaya, I.M. Pribytkova, YU.A. Ustynyuk, *J. Organomet. Chem.* 37 (1972) 187;
(b) B.L. Booth, G.C. Casey, *J. Organomet. Chem.* 178 (1979) 371;
(c) R. Blumhofer, K. Fischer, H. Vahrenkamp, *Chem. Ber.* 119 (1986) 194;
(d) H. Lehmkuhl, C. Krüger, S. Pasykiewicz, J. Popławska, *Organometallics* 7 (1988) 2038;
(e) S. Pasykiewicz, A. Pietrzykowski, L. Trojanowska, P. Sobota, L. Jerzykiewicz, *J. Organomet. Chem.* 550 (1998) 111.
- [4] (a) See for example: S. Stella, C. Floriani, A. Chiesi-Villa, C. Guastini, *New J. Chem.* 12 (1988) 621;
(b) H. Wadepohl, H. Pritzkow, *J. Organomet. Chem.* 450 (1993) 9;
(c) E.M. Holt, K.H. Whitmire, D.F. Shriver, *J. Am. Chem. Soc.* 104 (1982) 5621;
(d) L. Busetto, M. Green, B. Hessner, J.A.K. Howard, J.C. Jeffery, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1983) 519;
(e) E. Roland, H. Vahrenkamp, *Organometallics* 2 (1983) 1048;
(f) J.C. Jeffery, M.J. Parrot, U. Pyell, F.G.A. Stone, *J. Chem. Soc., Dalton Trans.* (1988) 1121;
(g) J.T. Park, J.R. Shapley, M.R. Churchill, C. Bueno, *J. Am. Chem. Soc.* 105 (1983) 6182.
- [5] (a) M.G. Thomas, E.L. Muetterties, R.O. Day, V.W. Day, *J. Am. Chem. Soc.* 98 (1976) 4645;
(b) J.L. Davidson, M. Green, F.G.A. Stone, A.J. Welch, *J. Chem. Soc., Dalton Trans.* (1979) 506.
- [6] M.S. Paquette, L.F. Dahl, *J. Am. Chem. Soc.* 102 (1980) 6621.
- [7] A. Pietrzykowski, P. Buchalski, L. Jerzykiewicz, *J. Organomet. Chem.* 597 (2000) 133.
- [8] D.F. Evans, *J. Chem. Soc.* (1959) 2003.
- [9] S. Braun, H.O. Kalinowski, S. Berger, 150 and More Basic NMR Experiments, Wiley-VCH, 1998.
- [10] A. Haaland, *Acc. Chem. Res.* 12 (1979) 415.
- [11] A. Pietrzykowski, P. Buchalski, S. Pasykiewicz, J. Lipkowski, *J. Organomet. Chem.* 663 (2002) 249.
- [12] (a) D. Fenske, A. Hollnagel, K. Merzweiler, *Angew. Chem., Int. Ed. Engl.* 27 (1988) 65;
(b) D. Fenske, A. Hollnagel, *Angew. Chem., Int. Ed. Engl.* 28 (1989) 1390.
- [13] D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.* (1974) 133.
- [14] B.V. Nonius, "COLLECT" data collection software, 1998.
- [15] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), *Minor W. Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology*, vol. 276: *Macromolecular Crystallography, Part A*, Academic Press, New York, 1997, pp. 307–326.
- [16] G.M. Sheldrick, *SHELXS-97*, *Acta Crystallogr., Sect. A* 46 (1990) 467.
- [17] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [18] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.
- [19] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [20] W.J. Hehre, R. Ditchfield, J.A. Pople, *J. Chem. Phys.* 56 (1972) 2257.
- [21] E. Glendening, A.E. Reed, J.E. Carpenter, F. Weinhold, *NBO 3.1 Program Manual*, University of Wisconsin.