Rhodium Complexes of 3-Isocyano-1,2-dicarba-*closo*-dodecaborane(12): Crystal and Molecular Structure of (η^5-Pentamethylcyclopentadienyl)-1,2-dimethyl-3-isocyano-1,2-dicarba-*closo*-dodecaboran(12)ylrhodium(III) Dichloride

Leonid I. Zakharkin,* Valentina A. Ol'shevskaya, Aleksandr P. Pisarevsky, Aleksandr I. Yanovsky and Yurii T. Struchkov[†]

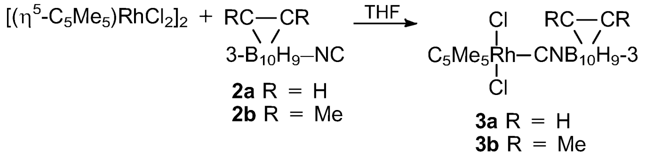
A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow, Russian Federation. Fax: +7 095 135 5085

Monomeric isocyano complexes of rhodium(III) have been prepared from 1,2-dimethyl-3-isocyano- **2b** and 3-isocyano-1,2-dicarba-*closo*-dodecaborane(12) **2a** and rhodium dimer $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ **1**; the structure of the resulting carborane rhodium complex was determined by an X-ray diffraction study.

Rhodium complexes are widely used as catalysts in various organic reactions.[1] The alkyl- and arylisocyano derivatives form an important class of rhodium derivatives; however, no data on isonitrile complexes with the cyano group bonded to a non-carbon atom have been as yet reported.

Earlier[2] we prepared 3-isocyano-1,2-dicarba-*closo*-dodecaborane(12) with the isocyano group bonded to the boron atom of the carborane cage. It was shown that such complexes exhibit essentially different chemical behaviour when compared to the organic isocyanides,[3] evidently due to specific steric characteristics.

In the present paper we report the synthesis and structure of previously unknown isocyanocarboranylrhodium(III) complexes obtained by the reaction of rhodium dimer $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ **1** with 3-isocyano- **2a** and 1,2-dimethyl-3-isocyano-1,2-dicarba-*closo*-dodecaborane(12) **2b** in THF.



$$[(\eta^5\text{-}C_5Me_5)RhCl_2]_2 + \begin{matrix} RC\text{—}CR \\ \backslash\ / \\ 3\text{-}B_{10}H_9\text{—}NC \end{matrix} \xrightarrow{THF} \begin{matrix} Cl & RC\text{—}CR \\ | & \backslash\ / \\ C_5Me_5Rh & \text{—}CNB_{10}H_9\text{-}3 \\ | & \\ Cl & \end{matrix}$$

2a R = H
2b R = Me

3a R = H
3b R = Me

The starting dimeric rhodium complex readily dissociates under the action of isocyanides **2a,b** and monomeric isocyanide derivatives of rhodium(III) **3a,b** are formed. Complexes **3a,b** are air-stable red-orange crystals; their solutions, however, are less stable. The structures of all complexes were confirmed by elemental analyses and IR spectroscopic data;[‡] an X-ray diffraction study was carried out for **3b**.[§]

Compound **3b** represents the first example of a structurally characterized organometallic complex with a 3-isocyano-carboranyl ligand. Moreover, so far no structural data at all have been available on isocyano-substituted carboranes, the only structurally-related compound studied being the decaborane thiocyanate derivative $6\text{-}B_{10}H_{13}NCS$.[4] On the other hand, some information on the molecular geometry of rhodium(I) and rhodium(III) complexes with substituted cyclopentadienyl and isocyanide ligands is available,[5–13] thus allowing us to compare the most important geometrical features of **3b** with those of the previously-studied isocyano rhodium derivatives.

The crystal structure of **3b** is composed of isolated $(C_5Me_5)(Me_2C_2B_{10}H_9NC)RhCl_2$ molecules (Fig. 1). The Rh–C(15) bond length of 1.937(3) Å is approximately in the

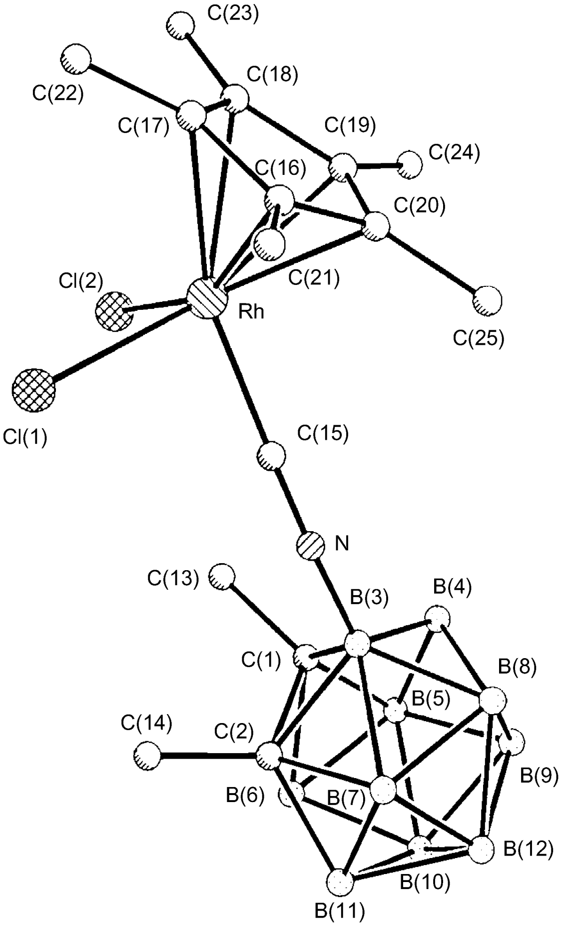


Fig. 1 Molecular structure of $C_{15}H_{30}B_{10}Cl_2NRh$ **3b**. Selected bond distances/Å and angles/°: Rh–Cl(1) 2.389(1), Rh–Cl(2) 2.395(1), Rh–C(15) 1.937(3), Rh–C(Cp*) 2.135–2.220, N–B(3) 1.458(5), N–C(15) 1.155(4), Cl(1)RhCl(2) 90.3(1), Cl(1)RhC(15) 90.4(1), Cl(2)RhC(15) 87.1(1), B(3)NC(15) 167.9(4), RhC(15)N 176.3(3).

[†] Professor Yurii Struchkov, Corresponding Member of the Russian Academy of Sciences, one of the leading scientists in the field of organic crystal chemistry, died on the 16th August 1995.

[‡] A solution of isocyanide **2a** or **2b** (1 mmol) in THF (5 ml) was added to a solution of **1** (0.5 mmol) in THF (25 ml). After being stirred for 30 min the THF was removed *in vacuo* and the residue was recrystallized from CH_2Cl_2–pentane. The yields of complexes **3a,b** were 95%.

3a: IR (KBr, ν/cm^{-1}): 2170 (NC), 2600 (BH). (Found: C 32.77, H 5.61, B 23.08%. Calc. for $C_{13}H_{26}B_{10}Cl_2NRh$: C 32.64, H 5.44, B 22.59%).

3b: IR (KBr, ν/cm^{-1}): 2168 (NC), 2600 (BH). (Found: C 35.84; H 5.77, B 21.40%. Calc. for $C_{15}H_{30}B_{10}Cl_2NRh$: C 35.57, H 5.92, B 21.34%).

[§] *Crystal data for* **3b**: $C_{15}H_{30}B_{10}Cl_2NRh$, $M = 506$, monoclinic, space group $P2_1/n$, $a = 7.827(2)$, $b = 26.917(8)$, $c = 11.482(4)$ Å, $\beta = 96.08(2)°$, $V = 2405(4)$ A , $Z = 4$, $D_c = 1.398$ g cm^{-3}. The X-ray diffraction experiment was carried out with a Siemens P3/PC diffractometer ($T = 192$ K, graphite-monochromated MoKα radiation, $\lambda = 0.71069$ A, $\theta-2\theta$ scan technique, $2\theta \leqslant 52°$.). The structure was solved by direct methods using SHELXTL PLUS programs (PC version). Anisotropic (isotropic for H atoms) least-squares refinement converged at $R = 0.0324$, $R_w = 0.0368$ for 3503 observed independent reflections with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, see *Mendeleev Commun.*, Notice to Authors, 1995, Issue 1.

middle of the range 1.86–1.98 Å observed in the previously-studied Rh complexes with isocyano ligands.[7–13] Two almost equal Rh–Cl bond lengths [2.389(1) and 2.395(1) Å] are well within the range of 2.33–2.45 Å reported for the chloro rhodium complexes.[6,9–12] The angles between the Rh–Cl(1), Rh–Cl(2) and Rh–C(15) bonds are close to 90°. It should be noted that the Cl(1)Cl(2)C(15) plane is almost parallel to the Cp* plane (dihedral angle 5.8°). Thus, if in accordance with the widely accepted tradition the Cp* group is considered as occupying three coordination sites, the coordination polyhedron of the Rh atom may be regarded as a distorted octahedron.

The RhC(15)NB(3) moiety is almost linear as in all previously reported isocyano Rh complexes:[5,7–13] angles at the C and N atoms in **3b** are equal to 176.3(3) and 167.9(4)°, respectively (the corresponding literature data 168–180° and 166–180°). The C–N bond length of 1.155(4) Å is within the usual range of 1.14–1.18 Å. It is interesting to note that the B–N bond in **3b** [1.458(5) Å] is essentially shorter than the 'standard' B–N bond (1.57 Å). Such increased bond order is quite common for B–N bonds and is observed when the lone electron pair of a nitrogen atom is not involved in other interactions. For example, in polyhedral borane and carborane molecules the B–NCS and B–NEt_2 bonds are as short as 1.435[4] and 1.427 Å,[14] respectively, whereas the B–$^{+}NEt_3$ bond is much longer (1.633 Å[15]).

The geometry of the carborane cage is unexceptional. The C–C, C–B and B–B bond lengths [1.686(5), 1.696(6)–1.729(6) and 1.756(6)–1.782(7) Å] are close to those reported in an earlier review.[16] The orientation of the carborane ligand in the crystal of **3b** may be characterized by a pseudo-torsion angle C(1)–B(3)–Rh–Cl(2) 4.0°. However, one would hardly expect there to be a considerable rotation barrier around the B–N bond; it is therefore quite probable that in solution more or less free rotation of the carborane nucleus can occur.

The authors gratefully acknowledge the financial support of the International Science Foundation (grant no. MO4000) and the Russian Foundation for Basic Research (grant no. 94-03-08338).

References

1 F. H. Jardine, *Stud. Inorg. Chem.*, 1991, **11**, 407.
2 L. I. Zakharkin, V. A. Ol'shevskaya and D. D. Sulaimankulova, *Metalloorg. Khim.*, 1992, **4**, 925 (*Organomet. Chem. USSR*, 1992, **4**, 449).
3 E. Singleton and H. E. Oosthuizen, *Adv. Organomet. Chem.*, 1983, **22**, 209.
4 D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 2915.
5 X. L. R.Fontaine, N. N. Greenwood, J. D. Kennedy, P. McKinnon and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 2809.
6 B. Cetinkaya, M. F. Lappert, G. M. McLaughlin and K. Turner, *J. Chem. Soc., Dalton Trans.*, 1974, 1591.
7 A. W. Hanson, A. J. McAlles and A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1985, 441.
8 D. T. Plummer, B. A. Rarcher, R. A. Jacobson and R. J. Angelici, *J. Organomet. Chem.*, 1984, **260**, 347.
9 W. D. Jones, R. P. Duttweiler and F. J. Feher, *Inorg. Chem.*, 1990, **29**, 1505.
10 Y. Yamamoto, K. Aoki and H. Yamazaki, *Inorg. Chem.*, 1979, **18**, 1681.
11 W. D. Jones and E. H. Hessell, *Organometallics*, 1990, **9**, 718.
12 Y. Yamamoto, Y. Wakatsuki and H. Yamazaki, *Organometallics*, 1983, **2**, 1604.
13 T. V. Ashworth, D. C. Liles, H. E. Oosthuizen and E. Singleton, *Acta Crystallogr., Sect. C*, 1984, **40**, 1169.
14 E. G. Ditzel, X. L. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1115.
15 C. F. Mitchell and A. J. Welch, *Acta Crystallogr., Sect. C*, 1986, **42**, 101.
16 V. S. Mastryukov, O. V. Dorofeeva and L. V. Vilkov, *Usp. Khim.*, 1980, **49**, 2377 (*Russ. Chem. Rev.*, 1980, **49**, 1181).

Received: Moscow, 17th March 1995
Cambridge, 7th June 1995; Com. 5/01752E