Mendeleev Communications

Mendeleev Commun., 2026, **36**, 28–30

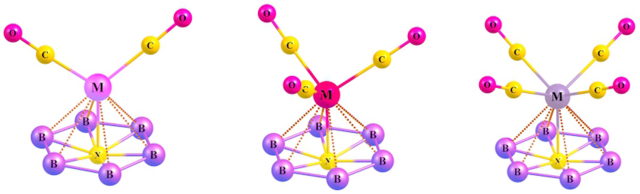
Metal carbonyl derivatives of CB_6 and NB_6 species: molecular rotors with hypercoordinated units

Tatyana N. Gribanova,* Ruslan M. Minyaev and Vladimir I. Minkin

Institute of Physical and Organic Chemistry, Southern Federal University, 344090 Rostov-on-Don, Russian Federation. E-mail: tngribanova@ipoc.sfedu.ru

DOI: 10.71267/mencom.7856

DFT calculations predict stability of 18-electron metal carbonyl derivatives of the CB_6 and CN_6 species, which represent a new structural type of metal coordination compounds with non-classical ligands containing a hypercoordinated central atom. These systems exist as mixtures of isoenergetic conformers associated with the rotation of metal carbonyl groups, thus being a kind of 'free rotors'.



$XB_6M(CO)_n$

X = C, N; M = V, Cr, Mn, Fe, Co, Ni; n = 2–4

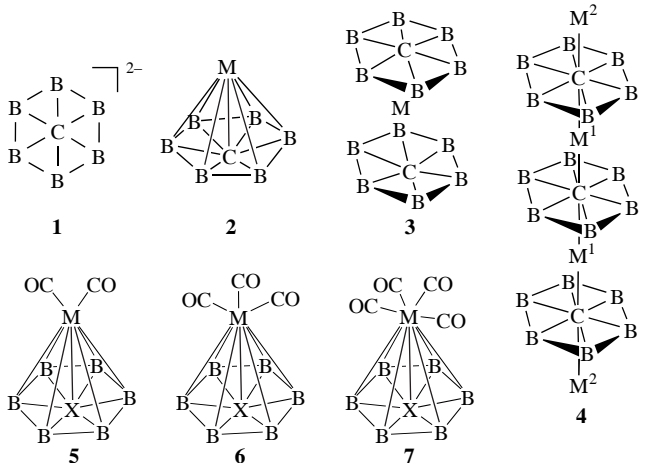
Keywords: hypercoordinate carbon, hypercoordinate nitrogen, CB_6 complexes, NB_6 complexes, pyramidal structures, metal carbonyl derivatives, rotation process, 18-electron rule, hypercoordination, molecular rotors.

Systems containing hypercoordinated carbon and other atoms attract much attention due to their unique electronic, optical and magnetic properties, which opens up opportunities for wide use of these systems in various fields of science and technology.[1,2] An effective strategy for stabilizing planar hypercoordinated centers is to include them in an appropriate boron environment.[1–10] The productivity of this approach, based on combined electronic and steric factors, has been confirmed by the discovery of numerous systems with hypercoordinated carbon, boron, nitrogen and other centers.[1,2,11–17]

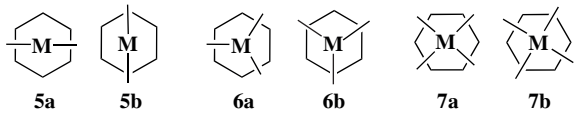
The simplest binary system with a planar hexacoordinated carbon atom in a boron environment is the dianion CB_6^{2-} **1**.[7] The unusual geometry of this system in the form of a wheel with a central hexacoordinated carbon atom determines specific magnetic and bonding characteristics, and makes it and its derivatives attractive candidates for synthetic searches.[6] The dianion CB_6^{2-} has an aromatic benzene-like 6π-electron system,[7] which ensures the stability of its non-classical structure. Stabilization of the CB_6 unit in the neutral form is achieved in various polycyclic compounds[2,6,18] and organometallic complexes,[19–22] where CB_6 plays the role of a ligand. Thus, according to theoretical studies, pyramidal **2**,[19] as well as sandwich **3** and multidecker sandwich **4** derivatives of both transition[20,22] and non-transition[19,21] metals can be formed on the basis of CB_6 and NB_6 structural units. The study of the possibilities of implementing non-classical systems as ligands in metal coordination compounds is expected to become a new area of research combining coordination chemistry and the chemistry of non-classical compounds.

A promising direction here is the study of metal carbonyl complexes of non-classical systems. As our previous studies have shown,[23,24] metal carbonyl substituents allow stabilizing various non-standard configurations and provide wide possibilities for varying their structure and properties. Within the framework of the described approach, in this work we used DFT methods to investigate the structures and stability of pyramidal metal carbonyl complexes based on CB_6 and NB_6 species of three structural types **5**–**7** (X = C, N; M = V, Cr, Mn, Fe, Co, Ni). By analogy with classical organometallic compounds, it can be expected that the rule of 18-electron stability will also be fulfilled in systems with non-classical fragments. Therefore, 14-electron ligands were chosen for CB_6 derivatives, and 13-electron ligands for NB_6 derivatives. The calculation procedure is described in Online Supplementary Materials.

In the case of dicarbonyl complexes **5** with carbon and nitrogen derivatives, the 18-electron rule is fulfilled in the $CB_6Ni(CO)_2$ and $NB_6Co(CO)_2$ systems, respectively. As shown by calculations at B3LYP and PBE0 levels, structures **5a** (C_{2v} symmetry) with a staggered conformation of the metal carbonyl fragment relative to the basal ring XB_6 correspond to energy minima ($\lambda = 0$), while systems **5b** (C_{2v} symmetry) with an eclipsed conformation correspond to first-order points ($\lambda = 1$) on the potential energy surfaces (PESs). The structural and energy parameters of the systems are presented in Figure 1 and Table S1 (see Online Supplementary Materials).



1 **2** **3** **4** **5** **6** **7**



5a **5b** **6a** **6b** **7a** **7b**

The basal XB_6 rings in the $CB_6Ni(CO)_2$ and $NB_6Co(CO)_2$ complexes are quasi-planar with slight pyramidalization of the hypercoordinated center X. The bond lengths of the central carbon atom with the boron environment in complex **5a** (X = C, M = Ni) are 1.603 (B3LYP)/1.609 (PBE0) Å, which is slightly longer than the lengths of the single C–B bonds (1.6 Å[25]). In complex **5a** (X = N, M = Co), the calculated N–B bond lengths are 1.613 (B3LYP)/1.619 (PBE0) Å. The calculated B···B distances along the perimeter of the XB_6 fragments in the complexes are in the range of 1.58–1.62 Å and are considerably shortened compared with the parameters of the single covalent B–B bonds (1.7 Å[25]).

The interatomic distances X···M are 1.998 (B3LYP)/1.961 (PBE0) Å in **5a** (X = C, M = Ni) and 1.917 (B3LYP)/1.885 (PBE0) Å in **5a** (X = N, M = Co), which slightly exceeds the sum of the covalent radii (1.92 Å for the C–Ni pair and 1.86 Å for the N–Co pair). At the same time, the calculated bond lengths of the central atom with the metal atom are in the range of experimental values for organometallic compounds: for example, the Ni–C distances in nickel complexes with alkenes are 1.921–2.064 Å,[26] and the Co–N bond lengths in various pyridine organocobalt complexes are in the range of 1.873–2.194 Å.[27]

Eclipsed conformations **5b** for the $CB_6Ni(CO)_2$ and $NB_6Co(CO)_2$ complexes correspond to transition states of rotation of the metal carbonyl fragments relative to the basal ring. The calculated rotation barriers are very low and amount to 0.25 (B3LYP)/0.28 (PBE0) kcal mol^{-1} for the carbon derivative and 0.08 (B3LYP)/0.14 (PBE0) kcal mol^{-1} for the nitrogen derivative.

For tricarbonyl derivatives **6**, the 18-electron rule is satisfied by the $CB_6Fe(CO)_3$ and $NB_6Mn(CO)_3$ complexes (see Figure 1 and Table S1). As in the case of dicarbonyl systems, the staggered conformations **6a** (C_{3v} symmetry) correspond to energy minima on the PES, while the eclipsed conformations **6b** (C_{3v} symmetry) correspond to first-order ($\lambda = 1$) stationary points on the PES.

The basal cycle of the $CB_6Fe(CO)_3$ and $NB_6Mn(CO)_3$ complexes retains a quasi-planar structure with a slight pyramidalization of the bonds with the central atom, which are somewhat elongated compared to the dicarbonyl species. The interatomic distances X···M are 2.021 (B3LYP)/1.984 (PBE0) Å in **6a** (X = C, M = Fe) and 1.968 (B3LYP)/1.931 (PBE0) Å in **6a** (X = N, M = Mn), which slightly exceeds the sum of the covalent radii (1.93 Å for the C–Fe pair and 1.87 Å for the N–Mn pair). At the same time, the calculated bond lengths of the central atom with the metal atom are in the range of experimental values for organometallic compounds: for example, the Fe–C distances in alkyl iron complexes can be around 2.015–2.063 Å,[28] and in manganese complexes with amines, the Mn–N distances are around 2.286–2.470 Å.[29]

As in the previous case, the eclipsed conformations **6b** correspond to transition states of the rotation process of the metal carbonyl fragments relative to the basal ring, which is characterized by a low energy barrier. The calculated rotation barriers are 0.27 (B3LYP)/0.38 (PBE0) kcal mol^{-1} for the carbon derivative and 0.36 (B3LYP)/0.42 (PBE0) kcal mol^{-1} for the nitrogen derivative.

In the case of tetracarbonyl complexes **7**, the 18-electron rule is fulfilled in the $CB_6Cr(CO)_4$ and $NB_6V(CO)_4$ systems. The symmetry features of the basal cycle and the tetracarbonyl fragment do not allow to form ideally staggered or ideally eclipsed conformations in this case, which leads to the formation

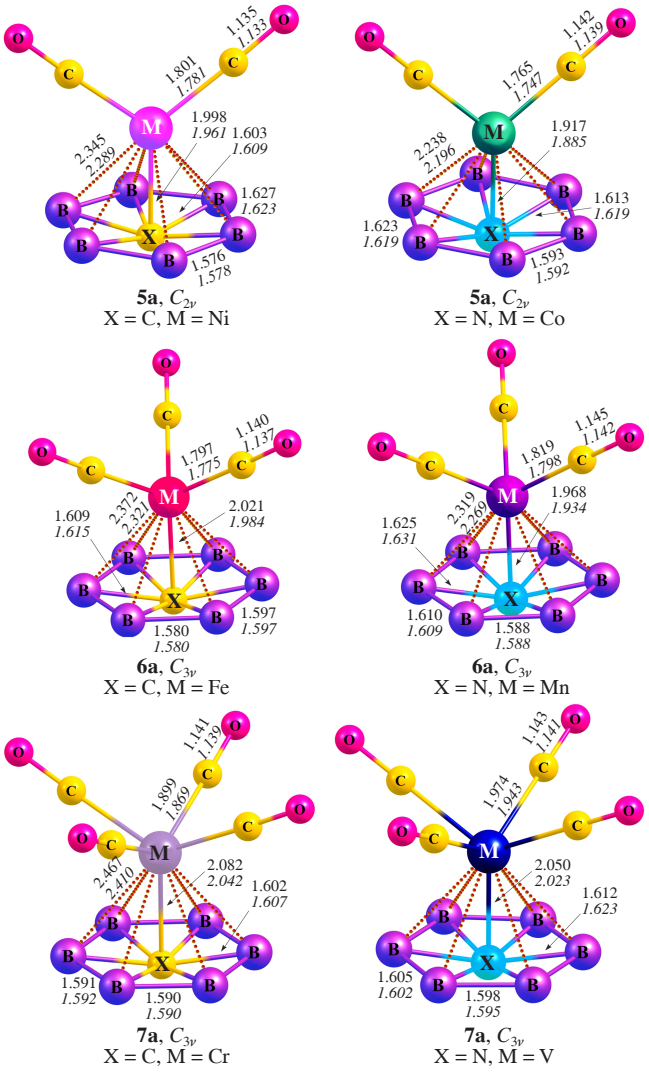


Figure 1 Bond lengths (Å) of systems **5a**, **6a** and **7a** calculated using the B3LYP (values in roman) and PBE0 (values in italics) methods with the 6-311+G(df) basis set.

of mixed forms. As calculations show, two types of structures **7a** and **7b** with C_{2v} symmetry correspond to energy minima and are energetically equivalent to the structure of the transition state with C_2 symmetry (see Figure 1 and Table S1). Thus, the rotation of apical groups relative to the basal cycle in tetracarbonyl complexes occurs freely (energy barrier = 0).

The interatomic distances X···M are 2.082 (B3LYP)/2.042 (PBE0) Å in **7a** (X = C, M = Cr) and 2.050 (B3LYP)/2.023 (PBE0) Å in **7a** (X = N, M = V), which is slightly larger than the sum of the covalent radii (1.95 Å for the C–Cr pair and 1.92 Å for the N–V pair). The calculated X–M bond lengths are in the range of experimental values for organometallic compounds: for example, in bis-alkynyl chromium complexes, the Cr–C bond lengths are around 2.059–2.078 Å,[30] and in vanadium complexes with triamidoamine ligands, the V–N bond lengths to amido nitrogens range in 1.896–1.928 Å, and the V–N bond to amine nitrogen is around 2.173–2.185 Å.[31]

According to the AIM[32] analysis (Figure S1 and Table S2), the central atom X in all the considered complexes forms six bond paths with the boron environment and a seventh additional bond path with the metal atom, thus being heptacoordinated. Each of the bond paths connecting the central atoms with the boron environment corresponds to the interaction with the B–B bond, rather than directly with individual boron atoms. As can be seen from Table S2, the critical points corresponding to C···B interactions are characterized by negative values of the electron

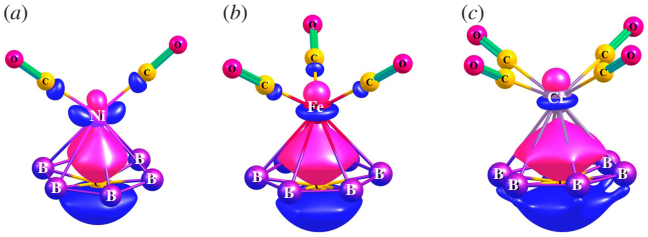


Figure 2 Shapes of molecular orbitals involved in the formation of C–M bonds in CB_6 complexes (*a*) **5**, (*b*) **6** and (*c*) **7**.

Laplacian $\nabla^2\rho(r)$, fairly high values of the charge density $\rho(r)$, a negative sign of the total energy density $H(r)$ and a ratio of the kinetic and potential energy densities $-G(r)/V(r)$ below 0.5, which together indicate a predominantly covalent nature of the C–B bonds. For critical points of the bond paths corresponding to N···B interactions, the Laplacian values of the electron density are positive, and the ratio $-G(r)/V(r)$ exceeds 0.5, which indicates an increase in the ionic contribution to the bonding of the central atom with the boron environment in the NB_6 derivatives compared to the CB_6 derivatives.

For X···M interactions, the calculated AIM parameters [positive value of the Laplacian, low electron density at the critical point and the $-G(r)/V(r)$ ratio in the range of 0.8–0.9] indicate an ionic nature of the bonding, which, according to molecular orbital analysis data, is provided by the interaction of the d_z^2 orbital of the metal atom and the p_z orbital of the central atom (Figure 2). As in the case of metal carbonyl compounds with hydrocarbon rings,[23,33,34] an important factor in the stabilization of complexes **5**–**7** is metalloaromaticity.[35–37] Metal carbonyl fragments, being donors of one (for NB_6 complexes) or two (for CB_6 complexes) electrons,[23] ensure the formation of the aromatic basal cycles XB_6, similar to the dianion CB_6^{2-}.[7]

Thus, our calculations show that non-classical CB_6 and CN_6 species are capable of forming metal carbonyl complexes of various compositions, the stabilization condition of which is the fulfillment of the 18-electron rule. The complexes, which represent a new structural type of coordination compounds, are stabilized by an additional, seventh, bond of the central atom and exist as a mixture of isoenergetic conformers associated with the rotation of metal carbonyl groups and separated by insignificant barriers, being a kind of 'free rotors'.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (State assignment in the field of scientific activity, project no. FENW-2023-0017).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7856.

References

1 V. I. Minkin, R. M. Minyaev and R. Hoffmann, *Russ. Chem. Rev.*, 2002, **71**, 869; https://doi.org/10.1070/RC2002v071n11ABEH000729.
2 L.-M. Yang, E. Ganz, Z. Chen, Z.-X. Wang and P. von Ragué Schleyer, *Angew. Chem., Int. Ed.*, 2015, **54**, 9468; https://doi.org/10.1002/anie.201410407.
3 R. M. Minyaev and T. N. Gribanova, *Russ. Chem. Bull.*, 2000, **49**, 783; https://doi.org/10.1007/BF02494697.
4 R. M. Minyaev, T. N. Gribanova, A. G. Starikov and V. I. Minkin, *Mendeleev Commun.*, 2001, **11**, 213; https://doi.org/10.1070/MC2001v011n06ABEH001496.
5 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Mendeleev Commun.*, 2001, **11**, 169; https://doi.org/10.1070/MC2001v011n05ABEH001461.
6 K. Ito, Z. Chen, C. Corminboeuf, C. S. Wannere, X. H. Zhang, Q. S. Li and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 2007, **129**, 1510; https://doi.org/10.1021/ja067292+.
7 K. Exner and P. von Ragué Schleyer, *Science*, 2000, **290**, 1937; https://doi.org/10.1126/science.290.5498.1937.
8 B. B. Averkiev, L.-M. Wang, W. Huang, L.-S. Wang and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2009, **11**, 9840; https://doi.org/10.1039/B908973J.
9 K. Ito, Z. Pu, Q.-S. Li and P. von Ragué Schleyer, *Inorg. Chem.*, 2008, **47**, 10906; https://doi.org/10.1021/ic800993b.
10 B. B. Averkiev and A. I. Boldyrev, *Russ. J. Gen. Chem.*, 2008, **78**, 769; https://doi.org/10.1134/S1070363208040361.
11 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Russ. J. Gen. Chem.*, 2008, **78**, 750; https://doi.org/10.1134/S107036320804035X.
12 R. Islas, T. Heine, K. Ito, P. v. R. Schleyer and G. Merino, *J. Am. Chem. Soc.*, 2007, **129**, 14767; https://doi.org/10.1021/ja074956m.
13 Z. Pu, K. Ito, P. v. R. Schleyer and Q.-S. Li, *Inorg. Chem.*, 2009, **48**, 10679; https://doi.org/10.1021/ic901377h.
14 C. Hu, S.-J. Gao, F.-L. Liu and H.-J. Zhai, *Chem. – Asian J.*, 2025, **20**, e00615; https://doi.org/10.1002/asia.202500615.
15 Y. Liao, C. L. Cruz, P. von Ragué Schleyer and Z. Chen, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14898; https://doi.org/10.1039/C2CP41521F.
16 C. Romanescu, T. R. Galeev, A. P. Sergeeva, W.-L. Li, L.-S. Wang and A. I. Boldyrev, *J. Organomet. Chem.*, 2012, **721**–**722**, 148; https://doi.org/10.1016/j.jorganchem.2012.07.050.
17 S. A. Zaitsev, I. V. Getmanskii, T. N. Gribanova and R. M. Minyaev, *Mendeleev Commun.*, 2025, **35**, 123; https://doi.org/10.71267/mencom.7595.
18 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Mendeleev Commun.*, 2022, **32**, 298; https://doi.org/10.1016/j.mencom.2022.05.002.
19 Q. Luo, X. H. Zhang, K. L. Huang, S. Q. Liu, Z. H. Yu and Q. S. Li, *J. Phys. Chem. A*, 2007, **111**, 2930; https://doi.org/10.1021/jp067853j.
20 S.-D. Li, J.-C. Guo, C.-Q. Miao and G.-M. Ren, *Angew. Chem., Int. Ed.*, 2005, **44**, 2158; https://doi.org/10.1002/anie.200462476.
21 L.-M. Yang, H.-P. He, Y.-H. Ding and C.-C. Sun, *Organometallics*, 2008, **27**, 1727; https://doi.org/10.1021/om7008588.
22 S.-D. Li, C.-Q. Miao and J.-C. Guo, *J. Phys. Chem. A*, 2007, **111**, 12069; https://doi.org/10.1021/jp076006t.
23 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Open Org. Chem. J.*, 2011, **5**, 62; https://doi.org/10.2174/1874364101105010062.
24 T. N. Gribanova, R. M. Minyaev, V. I. Minkin and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2018, **20**, 27830; https://doi.org/10.1039/C8CP05444D.
25 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 186; https://doi.org/10.1002/chem.200800987.
26 F. J. Ritz, L. Valentin, A. Henss, C. Würtele, O. Walter, S. I. Kozhushkov, A. de Meijere and S. Schindler, *Eur. J. Org. Chem.*, 2021, 1864; https://doi.org/10.1002/ejoc.202100045.
27 M. F. Summers, P. J. Toscano, N. Bresciani-Pahor, G. Nardin, L. Randaccio and L. G. Marzilli, *J. Am. Chem. Soc.*, 1983, **105**, 6259; https://doi.org/10.1021/ja00358a012.
28 S. M. Bhutto, R. X. Hooper, S. F. McWilliams, B. Q. Mercado and P. L. Holland, *Chem. Sci.*, 2024, **15**, 3485; https://doi.org/10.1039/D3SC05939A.
29 J. Glerup, P. A. Goodson, D. J. Hodgson, N. Jensen and K. Michelsen, *Bull. Chem. Soc. Ethiop.*, 2004, **18**, 17; https://doi.org/10.4314/bcse.v18i1.61632.
30 A. J. Schuman, M. M. Mills, L. Rodriguez Segura, L. A. Miller-Clark and T. Ren, *J. Organomet. Chem.*, 2021, **954**–**955**, 122110; https://doi.org/10.1016/j.jorganchem.2021.122110.
31 Y. Kokubo, I. Igarashi, K. Nakao, W. Hachiya, S. Kugimiya, T. Ozawa, H. Masuda and Y. Kajita, *Molecules*, 2022, **27**, 5864; https://doi.org/10.3390/molecules27185864.
32 R. F. W. Bader, *Acc. Chem. Res.*, 1985, **18**, 9; https://doi.org/10.1021/ar00109a003.
33 T. N. Gribanova, R. M. Minyaev, A. G. Starikov and V. I. Minkin, *Russ. Chem. Bull.*, 2009, **58**, 691; https://doi.org/10.1007/s11172-009-0080-9.
34 T. N. Gribanova, R. M. Minyaev and V. I. Minkin, *Phys. Chem. Chem. Phys.*, 2012, **14**, 14803; https://doi.org/10.1039/C2CP41839H.
35 B. E. Bursten and R. F. Fenske, *Inorg. Chem.*, 1979, **18**, 1760; https://doi.org/10.1021/ic50197a007.
36 J. W. Chinn, Jr. and M. B. Hall, *Inorg. Chem.*, 1983, **22**, 2759; https://doi.org/10.1021/ic00161a023.
37 H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1956, 1969; https://doi.org/10.1039/JR9560001969.

Received: 24th June 2025; Com. 25/7856