Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2019, **29**, 573–574

Mendeleev Communications

New bis-rhodium complex with a bidentate 3-phosphino-1,2,3,6-tetrahydrophosphinine P-ligand

Irina L. Odinets,[a] Tamás Körtvélyesi,[b] Réka Herbay,[c] Péter Bagi[c] and György Keglevich*[c]

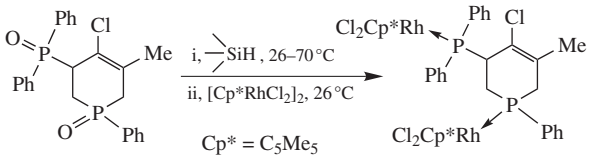
[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

[b] *Department of Physical Chemistry, University of Szeged, 6701 Szeged, Hungary*

[c] *Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary. E-mail: gkeglevich@mail.bme.hu*

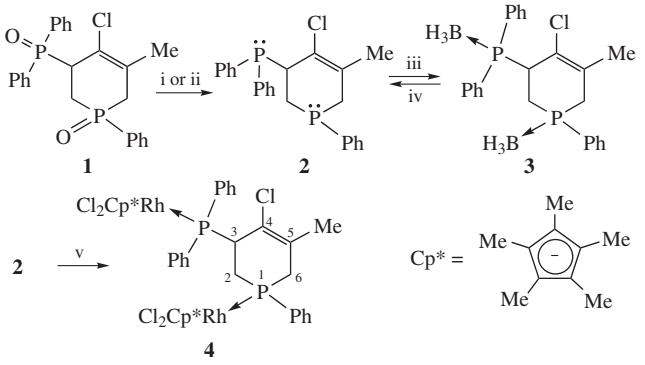
DOI: 10.1016/j.mencom.2019.09.032

Reaction between the title bidental P-ligand (obtained from 4-chloro-5-methyl-1-phenyl-3-diphenylphosphoryl-l,2,3,6-tetrahydrophosphinine oxide by double deoxygenation using trichlorosilane or phenylsilane) and two equivalents of $(Me_5C_5)RhCl_2$ led to the corresponding bis-Rh^{III} complex whose structure was evaluated by *ab initio* and DFT calculations. Attempts to achieve selective complexation of either the ring or exocyclic P-function were unsuccessful.



Heterocyclic P^{III} derivatives form a special class of P-ligands that can be used in complexation with transition metals such as platinum, palladium and rhodium.[1] As regards Rh^{III} complexes, (2,4,6-trialkylphenyl)phosphole,[2] 3-aryl-3-phosphabicyclo[3.1.0]hexanes and 1,2-dihydrophosphinine[3,4] were described as heterocyclic P-ligands. In the sphere of Pt^{II} complexes, we used arylphospholes, dibenzo[*c*.*e*][l,2]oxaphosphorines or dibenzooxaphosphorine-related biaryls, as well as phospholenes, phosphabicyclo[3.1.0]hexanes and dihydrophosphinines as complexants.[5,6] Optically active 3-phospholene-platinum complexes were also prepared.[7] 3-Diphenylphosphino-l,2,3,6-tetrahydro- and 1,2,3,4,5,6-hexahydrophosphinines served as bidental P-ligands in complexation with dichloro(dibenzonitrile)platinum to give the corresponding *cis*-chelate complexes.[8,9] In this communication, the possibilities for the complexation of 3-diphenylphosphino-substituted 1,2,3,6-tetrahydrophosphinine with $(Me_5C_5)RhCl_2$ are considered on experimental and theoretical bases.

3-Diphenylphosphoryl-l,2,3,6-tetrahydrophosphinine oxide **1**, available from an earlier study[8], after double deoxygenation may serve as a useful bidentate P-ligand. The reduction can be accomplished under 'classical conditions' involving trichlorosilane/pyridine in boiling benzene[10] as was done during the preparation of the corresponding *cis*-chelate Pt^{II} complex.[9] However, the required bis-phosphine **2** can be obtained in a more clear-cut way if the reduction is carried out with trichlorosilane at 0–26 °C (Scheme 1). The third possibility was to perform the deoxygenation with phenylsilane at 70 °C in a bomb. Due to its high sensitivity towards air, it was better to utilize bis-phosphine **2** immediately, or to convert it to suitable for storage bis-borane complex **3** upon treatment with $Me_2S{\cdot}BH_3$ (see Scheme 1).†



Scheme 1 *Reagents and conditions:* i, Cl_3SiH, PhH, 0–26 °C; ii, $PhSiH_3$, 70 °C; iii, $Me_2S{\cdot}BH_3$, CH_2Cl_2/THF, 26 °C; iv, Et_2NH, PhH, boiling; v, $[(Me_5C_5)RhCl_2]_2$, CH_2Cl_2, 26 °C.

It is easy to liberate bis-phosphine **2** from complex **3** by boiling it with diethylamine in benzene.[11] Bis-phosphine **2** obtained by the reduction of bis-oxide **1** readily reacted with two equivalents of $(Me_5C_5)RhCl_2$ at 26 °C in dichloromethane to afford bis-Rh^{III} complex **4**‡ (see Scheme 1). The new complex **4** was characterized by ^{31}P, ^{13}C and ^{1}H NMR spectral data. The two $J_{P–Rh}$ couplings of 130.6 and 133.4 Hz observed in the ^{31}P NMR spectrum of product

† *4-Chloro-3-diphenylphosphino-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine* **2**. *Method A*. Bis(phosphine oxide) **1**[8] (61 mg, 0.14 mmol) in benzene (1 ml) was degassed by nitrogen, and the solution was cooled to 0 °C. Trichlorosilane (0.056 ml, 0.56 mmol) was then added, and the mixture was stirred at 0 °C for 3 h, and then at 26 °C for another 3 h under nitrogen. Evaporation of the solvent gave crude bis-phosphine **2** in a quantitative yield (~57 mg). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ: –4.7 (P^1), –26.0 (P–C^3), $^3J_{PP}$ 43.0 Hz. *Method B*. Bis(phosphine oxide) **1** (61 mg, 0.14 mmol) and phenylsilane (0.10 ml, 0.84 mmol) were heated at 70 °C under nitrogen in a sealed tube for 3 days.

4-Chloro-3-diphenylphosphino-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine *P*,*P*′-bis-(borane) complex **3** was prepared as described earlier.[9] ^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 6.6 and 30.3 (broad signals), similar to reported;[9] ^{11}B NMR (160.4 MHz, $CDCl_3$) δ: –35.4 and –38.1 (broad signals).

‡ *(4-Chloro-3-diphenylphosphino-5-methyl-1-phenyl-1,2,3,6-tetrahydrophosphinine*-P,P′*)bis[dichloro(pentamethylcyclopentadienyl)-rhodium(III)]* **4**. Crude bis-phosphine **2** (0.14 mmol) obtained by method A or B was taken up in degassed CH_2Cl_2 (3 ml). The solution was cooled to 0 °C, and $(Me_5C_5)RhCl_2$ (87 mg, 0.14 mmol) in degassed CH_2Cl_2 (4 ml) was added within 10 min. The solution was stirred at 26 °C for 1 h, the solvent

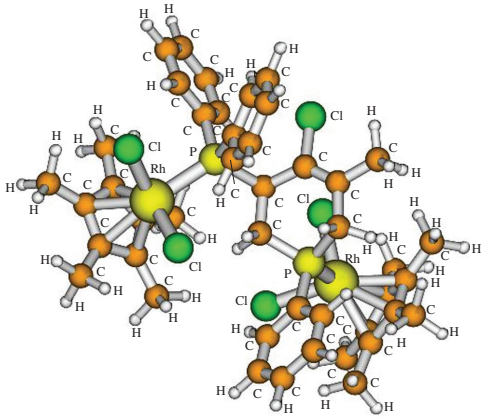


Figure 1 Stereostructure of bis-Rh^{III} complex **4** obtained by B3LYP/6-31G* and LANL2DZ ECP.

4 as well as the signals of two Me_5C_5 moieties in the ^{1}H NMR spectrum confirmed the double complexation. Unfortunately, complex **4** was not stable, and started decomposing in a few hours after the preparation.

The structure of complex **4** was elucidated by *ab initio*, and then B3LYP/6-31G* calculations for the C, H, P and Cl atoms and LANL2DZ ECP calculations for the Rh atoms[§] (Figure 1). It can be noticed that the conformation of the hetero ring changed on double complexation. On the basis of earlier investigations[9] stating that the 3-Ph_2P-l,2,3,6-tetrahydrophosphinine **2** cycle exists in the twist-boat conformation, on Rh-complexation the tetrahydrophosphinine ring took up a twist chair conformation as the best one found on the potential surface. Accoding to our earlier experiences, the stereostructures and the geometrical data of the transition metal complexes may be adequately described by the B3LYP/6-31G*–LANL2DZ ECP calculations applied.[12] The calculated geometrical data and the spatial structure of complex [*cis*-bis(ethoxydibenzooxaphosphorino)$PtCl_2$][13] were well validated by the X-ray measurement carried out later on a suitable single crystal of the methoxy analogue.[14] Another example of validation may be the agreement on the stereostructure of the starting 3-phosphinoyl-1,2,3,6-tetrahydrophosphinine oxide **1** in the gas and in the solid phase evaluated by calculations[15] and X-ray,[8] respectively.

Bis-phosphine **2** was also reacted with one equivalent of $(Me_5C_5)RhCl_2$, however no selective complexation leading either to the l-phenyltetrahydrophosphinine-Rh^{III} complex or to the (3-tetrahydrophosphininyl)diphenylphosphine-Rh^{III} complex could be observed. Instead, the same bis-complex **4** was formed but in a lower yield. Theoretical calculations justified that no significant selectivity in the complexation of any of the P^{III} centers in bis-phosphine **2** can be expected. The difference between the relative energies of the species formed by complexation on P(1) and on the exocyclic P-moiety of bis-phosphine **2** is 6.1 kcal mol^{-1}, suggesting that the P(1) center is somewhat more reactive.

In summary, a new bis-Rh^{III} complex adopting a *twist chair* conformation was prepared by double deoxygenation of 3-diphenylphosphoryl-l,2,3,6-tetrahydrophosphinine oxide followed by the complexation with dimeric $(Me_5C_5)RhCl_2$. Selective complexation was not possible at either of the P^{III}-centers.

In memory of the late Professor Irina Odinets recalling our joint works and friendship. The research was supported by the National Research, Development and Innovation Office (K119202).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.032.

References

1 F. Mathey, in *Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain*, ed. F. Mathey, Pergamon, Amsterdam, 2001, ch. 7, p. 753.
2 I. Odinets, T. Körtvélyesi, T. Kégl, L. Kollár and G. Keglevich, *Transition Met. Chem.*, 2007, **32**, 299.
3 I. L. Odinets, N. M. Vinogradova, K. A. Lyssenko, D. G. Golovanov, P. V. Petrovskii, T. A. Mastryukova, H. Szelke, N. Balázsdi Szabó and G. Keglevich, *J. Organomet. Chem.*, 2005, **690**, 704.
4 I. L. Odinets, N. M. Vinogradova, E. V. Matveeva, D. D. Golovanov, K. A. Lyssenko, G. Keglevich, L. Kollár, G.-V. Roëschenthaler and T. A. Mastryukova, *J. Organomet. Chem.*, 2005, **690**, 2559.
5 M. S. Holt, J. J. MacDougall, F. Mathey and J. H. Nelson, *Inorg. Chem.*, 1984, **23**, 449.
6 G. Keglevich and L. Kollár, *Lett. Org. Chem.*, 2010, **7**, 612.
7 G. Keglevich, P. Bagi, E. Bálint and T. Körtvélyesi, in *Platinum: Compounds, Production and Applications*, eds. L. Varennikov and E. Yedemsky, Nova Science Publishers, New York, 2013, pp. 83–102.
8 G. Keglevich, M. Sipos, D. Szieberth, L. Nyulászi, T. Imre, K. Ludányi and L. Tőke, *Tetrahedron*, 2004, **60**, 6619.
9 G. Keglevich, M. Sipos, D. Szieberth, G. Petöcz and L. Kollár, *J. Organomet. Chem.*, 2004, **689**, 3158.
10 L. D. Quin, K. C. Caster, J. C. Kisalus and K. A. Mesch, *J. Am. Chem. Soc.*, 1984, **106**, 7021.
11 Y. Gourdel, A. Ghanimi, P. Pellon and M. Le Corre, *Tetrahedron Lett.*, 1993, **34**, 1011.
12 A. Kerényi, V. Kovács, T. Körtvélyesi, K. Ludányi, L. Drahos and G. Keglevich, *Heteroat. Chem.*, 2010, **21**, 63.
13 G. Keglevich, A. Kerényi, B. Mayer, T. Körtvélyesi and K. Ludányi, *Transition Met. Chem.*, 2008, **33**, 505.
14 T. Holzbauer, G. Keglevich, A. Kerényi and M. Czugler, *Acta Crystallogr., Sect. E: Crystallogr. Commun.*, 2009, **65**, m347.
15 M. Czugler, T. Körtvélyesi, L. Fábián, M. Sipos and G. Keglevich, *CrystEngComm*, 2007, **9**, 561.
16 *PcModel, Version 7.0*, Serena Software, Bloomington, IN, USA.
17 J. J. P. Stewart, *MOPAC2007*, USA, 2007.
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. Kiene, 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 and J. A. Pople, *Gaussian 03, Revision D.02*, Gaussian, Wallingford, CT, 2004.

Received: 28th May 2019; Com. 19/5936

was evaporated, and the crude product was purified by recrystallization from a mixture of degassed dichloromethane (4 ml) and pentane (4 ml). The solution was allowed to stand at 0 °C for 3 h. The red crystals precipitated were filtered and dried *in vacuo* to give 0.10 g (72%) of complex **4**. ^{31}P NMR (202.4 MHz, $CDCl_3$) δ: 36.2 (dd, P-1, $^1J_{Rh-P}$ 130.6 Hz, $^3J_{P-P}$ 37.8 Hz), 57.9 (dd, C^3–P, $^1J_{Rh-P}$ 133.4 Hz, $^3J_{P-P}$ 38.0 Hz). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.30–1.31 (m, 30H, Me_5–C_5), 1.84 (br.s, 3H, C^5–Me), 2.45 (br.dt, 1H, C^6H, *J* 44.7, *J* 11.4 Hz), 2.94–3.02 (m, 2H, C^6H and C^2H), 3.38 (br.t, 1H, C^2H, *J* 17.0 Hz), 3.87 (br.d, 1H, C^3H, *J* 46.4 Hz), 7.36–7.77 (m, 15H, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ: 9.1 (*Me*$_5$–C_5), 23.0 (C^5–*Me*), 30.3–30.8 (C^2, C^6), 43.9–44.3 (C^3), 103.3 (Cp*C), 126.2–135.5 (C^4, C^5 and Ar).

§ *Calculations.* Molecules were built up and preoptimized by PcModel.[16] The structures were reoptimized by the semiempirical quantum-chemical method PM6 implemented in MOPAC2007.[17] The geometry of optimized structures were reoptimized at the level of HF (Hartree–Fock) and B3LYP (DFT) using 6-31G* basis set for C, H, P, Cl atoms and LANL2DZ ECP (Effective Core Potential) for Rh atom(s).[18] The force matrices of the geometry in the minima were checked and found to be positive definite in the conformational analysis.