A Novel Five-Coordinate Rhodium(I) Complex

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An unusual five-coordinate isomer of the mononuclear complex $[Rh(CO)_2(PPh_3)_2I]$ has been isolated, and its crystallographic structure determined. The molecule has a slightly distorted trigonal-bipyramidal structure, with both PPh_3 ligands being in axial positions. A combination of IR and NMR spectroscopy with the results of DFT calculations shows that the complex maintains the same structure in solution.

Introduction

The adventitious detection[1] of $[Rh(CO)_2(PPh_3)_2Br]$ as a probable product of the reaction of $[Rh_6(CO)_{15}(PPh_3)]$ with Br^- led us to attempt to confirm its structure indirectly by crystallography of its more stable iodo analogue $[Rh(CO)_2(PPh_3)_2I]$ (**1**). This has been prepared more conveniently by reaction of $[Rh_4(CO)_{12}]$ with PPh_3 and NBu_4I under CO, and has been fully characterized by crystallography, IR and NMR spectroscopy. Five-coordinate $[Rh(CO)_2(PR_3)_2(Hal)]$ rhodium complexes had previously been reported[2–5] but were characterized only by NMR and IR spectroscopy. The spectroscopic data obtained for these complexes were not in good agreement but they are all compatible with four symmetrical structures described below. Two structures are based on a trigonal-bipyramidal motif[2–5] with either two COs or two phosphane ligands in the axial positions. Two other possibilities are represented by tetragonal pyramids with *cis* and *trans* arrangement of the ligands in the basal plane.[5] The disagreements in the experimental NMR spectroscopic data can be partially explained by fast exchange between the isomeric species[5] or by dissociative equilibria with the parent square planar $[Rh(CO)(PPh_3)_2(Hal)]$ complexes.[4]

The importance of a clear assignment of the structures of this sort lies in the general significance of five-coordinate Rh^I complexes in terms of the boundary between four-coordinate planar and five-coordinate (usually trigonal bipyramidal, sometimes square pyramidal) d^8 complexes in general, and their occurrence as intermediates in associative substitution reactions of planar Rh^I complexes and in similar reactions proposed for catalytic systems.[6] In particular, it has been clearly shown[5] that occurrence of the $[Rh(CO)_2(PPh_3)_2(Hal)]$ species must be taken into account in catalytic systems that contain the starting square-planar $[Rh(CO)(PPh_3)_2Hal]$ complexes under CO, a typical situation for carbonylation catalysis.

This aspect of the complex's importance is that there are only *two* other five-coordinate Rh^I complexes, the structures of which have been reported quite recently in the Cambridge Structural Database. One is the not exactly analogous $[Rh(PR_3)_2(CO)_3]^+$ cation[7] (trigonal-bipyramid with *trans* P donors), and the other is a closely analogous dinuclear $[Rh(CO)_2X(PP)]_2$ neutral complex, where two Rh^I centers are bridged by two long-chain bidentate diphosphane (PP) ligands. This has a trigonal-bipyramidal structure, with *trans* P donors. In general five-coordinate complexes of Rh^I are rare and/or unstable towards loss of the 5th ligand. In this paper we describe the isolation and detailed characterization (X-ray crystallography, IR, NMR) of the $[Rh(CO)_2(PPh_3)_2I]$ complex. The DFT optimization of the structure, and calculation of the IR spectroscopic characteristics are presented.

Results

The five-coordinate $[Rh(CO)_2(PPh_3)_2I]$ (**1**) complex, can be obtained either by addition of CO to the square-planar $[Rh(CO)(PPh_3)_2I]$[3] or by disproportionation of $[Rh_6(CO)_{15}(PPh_3)]$ in the presence of I^-.[1] In this paper we suggest another high-yield synthesis of **1** by the reaction of $[Rh_4(CO)_{12}]$ with I^- and PPh_3 under CO, according to the proposed stoichiometry:

$$3\,[Rh_4(CO)_{12}] + 4\,PPh_3 + 4\,I^- = 2\,[Rh_5(CO)_{15}I]^{2-} + 2\,[Rh(CO)_2(PPh_3)_2I]$$

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The complex is relatively stable in the solid state but in solution it must be kept under CO to prevent decarbonylation and formation of the square-planar [Rh(CO)(PPh$_3$)$_2$I] complex as was observed earlier.[3] The solid-state structure of **1** has been characterized by a single-crystal X-ray diffraction study. The IR, ^{31}P, ^{13}C and VT ^{1}H NMR spectroscopic characteristics of **1** in solution were also measured. A very good agreement of the NMR spectroscopic data obtained for **1** and those reported earlier[3] for [Rh(CO)$_2$(PPh$_3$)$_2$I] [^{31}P NMR: δ = 34.0 ppm, ^1J(Rh–P) = 91 Hz, ^{13}C: δ = 191.1 ppm, ^1J(Rh–C) = 70 Hz, ^2J(P–C), CD$_2$Cl$_2$, –50 °C] clearly indicates identity of these complexes. An ORTEP view of the molecule is shown in Figure 1 together with its principal structural parameters. The IR and ^{31}P NMR spectroscopic data are presented in the Experimental Section, and the mid-IR spectrum is shown in Figure 2. Quantum Chemical (DFT) calculations have been performed using the GAUSSIAN98 program package.[11] The DFT-B3LYP method,[12] and the basis set LanL2DZ with effective core potentials (ECP) for the Rh, P and I atoms,[13,14] were applied. The geometry optimizations were carried out without any symmetry constraints. The trigonal-bipyramidal structures with axial disposition of either phosphane or CO ligands were used as the starting geometries, but "no symmetry constraints" were imposed. Other feasible structures with the mixed axial/equatorial disposition of CO (PPh$_3$) ligands were not analyzed because they contradict the NMR spectroscopic data for **1**. In both cases we found local minima on the potential energy surface related to the corresponding structures. Selected results of these calculations are given in Table 1.

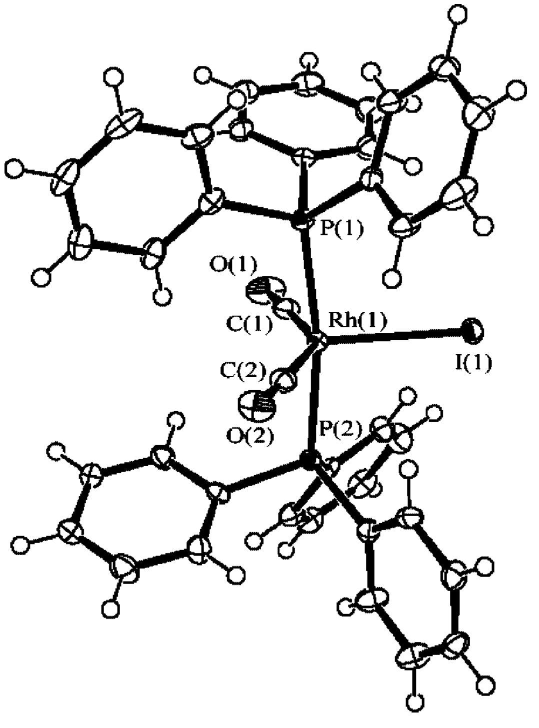

Figure 1. ORTEP plot of the molecular structure of [Rh(CO)$_2$(PPh$_3$)$_2$I] (**1**). Thermal ellipsoids are drawn at the 50% level. Selected bond lengths [Å], Rh(1)–P(1) 2.3385(8), Rh(1)–P(2) 2.3298(7), Rh(1)–C(1) 1.915(3), Rh(1)–C(2) 1.903(3), Rh(1)–I(1) 2.8241(3), O(1)–C(1) 1.148(3), O(2)–C(2) 1.144(3) and angles [°], P(2)–Rh(1)–P(1) 170.34(3), C(2)–Rh(1)–C(1) 143.46(13), C(2)–Rh(1)–I(1) 111.11(9), C(1)–Rh(1)–I(1) 105.42(9).

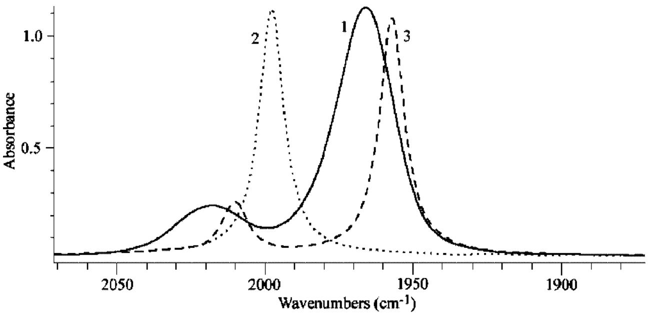

Figure 2. The IR spectroscopic patterns of the two trigonal-bipyramidal isomers of [Rh(CO)$_2$(PPh$_3$)$_2$I]. Experimental spectrum of **1** (–). Calculated spectra for the isomer with two axial (-----) and two equatorial (·····) PPh$_3$ ligands.

Discussion

In the solid state the molecule of **1** forms a trigonal pyramid with two phosphane ligands in the axial positions. The iodide and two carbonyl ligands occupy three equatorial sites. The molecule can be assigned to the C_{2v} idealized symmetry group. Two bonds connecting the phosphorus and rhodium atoms in **1** are slightly bent to form the angle of 170.34(3)°. This distortion from the idealized axial geometry of the phosphanes seems to be dictated by nonbonding interaction of the iodide with the phenyl substituents of the ligands. The angle between Rh–C(O) bonds in the equatorial plane [143.46(13)°] considerably exceeds the I–Rh–C(O) angles [111.11(9)° and 105.42(9)°] to accommodate the phenyl substituents tilted from the iodide to the carbonyl ligands because of the P–Rh–P angle distortion mentioned above. It is worth noting at this point that in the cobalt [Co(CO)$_2$(PEt$_3$)$_2$I][15] and iridium [Ir(CO)$_2$(PPh$_3$)$_2$I][16] congeners the angular distortions are minimal [e.g. P–Co–P and P–Ir–P angles equal to 179.0° and 179.1°, respectively] due to the smaller effective cone angle of the phosphane in the former complex, and to larger metal-to-ligands distances in the latter.

These distortions from an exact trigonal-bipyramidal conformation place **1** on the trajectory involved in a Berry rotation process of the sort usually invoked in scrambling reactions of trigonal-bipyramidal complexes. Because of this it is important to confirm that **1** exists in solution in the same isomeric form as that observed in the solid state. The ^{31}P NMR spectrum displays a doublet resonance (δ = 31.2 ppm [d, ^1J(Rh–P) 94.4 Hz]) that points to structurally equivalent phosphane ligands bound to rhodium. The ^{13}C{^{1}H} spectrum also displays one signal in the carbonyl region, split into doublet of triplets due to the couplings with rhodium [^1J(Rh–C) 70.0 Hz] and phosphorus [^2J(P–C) 14.5 Hz], the latter being typical of *cis* two-bond coupling. These data are compatible with two structural patterns,

Table 1. Selected experimental and calculated parameters for the two trigonal-bipyramidal isomers of $[Rh(CO)_2(PPh_3)_2I]$.

	Experimental	Calculated	
		Both PPh_3 ligands axial	Both PPh_3 ligands equatorial
E [a.u]		–1750.286712	–1750.284387
E + ZPE [a.u]		–1749.715615	–1749.713262
H_{298} [a.u]		–1749.672208	–1749.669831
G_{298} [a.u]		–1749.800687	–1749.798956
S [cal/(mol·K)]		270.408	271.766
ΔE [kcal/mol]		–1.46	
Bond lengths [Å]			
Rh–P	2.338; 2.330	2.450	2.526; 2.494
Rh–C	1.903; 1.916	1.906; 1.928	1.910; 1.916
Rh–I	2.824	2.962	2.888
C–O	1.147; 1.143	1.185; 1.181	1.175; 1.177
Bond angles [deg]			
(O)C–Rh–C(O)	143.4	142.4	168.5
P–Rh–P	170.3	177.6	124.4
IR carbonyl frequencies [cm^{-1}]			
$\nu_{antisym}$ (int., [km/mol])	1967 (1010)	1898 (1017)	1938 (1025)
$\nu_{antisym}$ corrected[a]		1956 (1017)	1997 (1025)
ν_{sym} (int.)	2022 (240)	1949 (225)	2001 (13)
ν_{sym} corrected[a]		2009 (225)	2062 (13)

[a] The values of band frequencies are multiplied by the scaling factor 1.03 (see text).

which contain either phosphane or carbonyl ligands in the axial positions of the trigonal bipyramid. Four signals of aromatic carbon atoms between δ = 133 and 128 ppm are indicative of free rotation of the phosphane ligands and their phenyl substituents about the P–C and Rh–P bonds. The proton spectra of **1** display two typical multiplets (2/3 relative intensities) of aromatic protons in the temperature range +25 °C to –40 °C (see Figure S1 in the supporting information; for details see also the footnote on the first page of this article) and this also points to the absence of steric hindrance to rotation in the molecule under these conditions. The latter observations make it more probable that the phosphane ligands are in the axial positions so that nonbonding interactions in the ligand sphere of **1** are minimized. Nevertheless, the NMR spectroscopic data do not allow an unambiguous decision on the stereochemistry of **1**. Analysis of the IR spectroscopic patterns corresponding to the alternative structural hypotheses (see below) showed that this type of spectroscopy provides more reliable background to make a choice in favor of one or another structure. The IR spectrum of **1** in the carbonyl region displays two bands of significant intensity (see Table 1) that is in contrast with the first report on the synthesis of $[Rh(CO)_2(PPh_3)_2I]$[3] where only one carbonyl absorption band was found. The NMR spectroscopic data for **1** are in a good agreement with the data obtained for the above compound[3] [$^{31}P\{^1H\}$ 34 ppm, $^{13}C\{^1H\}$ 191.1 ppm, ^1J(Rh–P) = 91 ppm, ^1J(Rh–C) = 70 Hz, ^2J(C–P) = 16 Hz], and it seems very probable that in the early study[3] the high-frequency band has been missed in the spectrum either because of low sensitivity of the instrument used or due to low concentration of the sample. It has to be also noted that structurally analogous complexes of cobalt[15] and iridium,[16] as well as the chloride and bromide rhodium derivatives[5] $\{[Rh(CO)_2(PPh_3)_2X]\}$ also display two absorption bands in the carbonyl region with essentially similar location and relative intensities. A very similar trigonal-bipyramidal environment of the Rh^I center has been recently found[17] in the dinuclear rhodium complex $[Rh(CO)_2I(PP)]_2$ where two rhodium atoms are bridged by a long-chain diphosphane (PP) ligand with the phosphorus functionalities in axial positions. The structure of this complex found in the solid state must be retained in solution because of the rigidity of the macrocyclic structure of this molecule and two carbonyl absorption bands observed in solution must be associated with the trigonal-bipyramidal structure bearing two phosphorus ligands in the axial positions. Thus the further analysis of geometry of **1** will be based on the presence of two carbonyl absorption bands in its IR spectrum, something that is evidently of crucial importance for a proper assignment of its solution structure.

The DFT calculations of the electronic structure of **1** have shown that the full energy of the isomer with *axial* PPh_3 ligands is slightly lower (1.5 kcal/mol) than that of the form with equatorial phosphanes. Although this small difference cannot be considered as a decisive argument in favor of one or another structure, it would allow for there being as little as ca. 10% of the equatorial isomer to be present in solution. Inclusion of thermochemical corrections does not change this ratio. The bond angles (Table 1), calculated for the isomer with two axial phosphane ligands, are in good agreement with the crystallographic data obtained for **1**. Higher values of the calculated Rh–C, Rh–I and C–O bonds are quite expected because polarizing functions were not included in the basis set of orbitals. Calculation of the IR spectra gave two carbonyl stretch bands (ν_{asymm} and ν_{symm}) for both isomeric forms with, however, essentially different relative intensities. Comparison of the calculated band frequencies with the experimental data shows considerable underestimation of the calculated values. However, this is quite typical for complexes of this sort, and an independent study[18] of another family of five-coordinate carbonyl rhodium compounds ([Rh(RCOO)(PPh$_3$)$_2$(CO)], R = H, CH$_3$, CF$_3$) showed that similar calculations gave consistent values of the band frequencies with the use of scaling factor equal to 1.03. When we applied this factor in the present study it led to much better agreement between experimental and calculated values of the band frequencies. However, in the present case these parameters alone do not allow distinguishing the two possible structures of **1**. Relative intensities of the bands are much stronger discriminative factor due to their well-documented dependence on the angle between carbonyl groups in dicarbonyl complexes.[6,16,19] The greater (O)C–Rh–C(O) bond angle when the CO ligands are both axial resulted in a decrease of the $I_{sym}/I_{antisym}$ value down to ca. 0.01, a value that would actually result in the disappearance of this band from the experimental spectrum. The agreement between experimental and calculated (O)C–Rh–C(O) bond angles when the phosphanes are both axial is completely in line with the excellent fit of the relative intensities of the calculated IR bands and those observed in the experimental spectrum, as shown in Figure 2. Thus, the combination of the spectroscopic data with the calculations described above allows an unambiguous assignment of the solution structure of **1**, which was arguable until the present time.

Experimental Section

General Comments: The complex [Rh$_4$(CO)$_{12}$] was prepared according to published procedure.[8] [NBu$_4$]I and PPh$_3$ (Aldrich) were used as received. Chloroform, hexanes and methanol (Aldrich) were used without additional purification. Tetrahydrofuran was distilled from over Na-benzophenone ketyl under nitrogen prior to use. Infrared spectra were recorded with a Nicolet Magna IR 550 FTIR spectrometer. ^{31}P, ^{1}H and ^{13}C NMR spectra were recorded with Varian Gemini 300 or Unity 500 instruments, and referenced to external 85% H$_3$PO$_4$ and residual solvent resonances, respectively.

Preparation of [Rh(CO)$_2$(PPh$_3$)$_2$I] (1): [Rh$_4$(CO)$_{12}$] (206 mg, 0.28 mmol) was dissolved in CHCl$_3$ (10 cm^3) and a slight excess of PPh$_3$ (97 mg, 0.37 mmol) was added to the solution under nitrogen. After the liberation of gaseous CO was complete, the reaction mixture was degassed (3 freeze-pump-thaw cycles) and saturated with CO. NBu$_4$I (184 mg, 0.5 mmol) was added to the solution under CO. The course of the reaction was monitored by ^{31}P NMR spectroscopy. After 6–7 hours the ^{31}P NMR spectrum displayed one doublet signal that indicated formation of a phosphorus-containing rhodium complex. The solvent was removed under a flow of gaseous CO. The resulting dark red oily material was first diluted with CO-saturated THF (1 cm^3) and then with CO-saturated methanol (10 cm^3) to give a yellow crystalline precipitate of [Rh(CO)$_2$(PPh$_3$)$_2$I] (**1**) and a dark red solution containing anionic cluster species. The suspension obtained was stirred under a flow of CO for 15 minutes to complete precipitation of the product. The mother liquor was then carefully decanted, and the residue was washed with CO-saturated methanol (2×3 cm^3) and dried under a flow of CO to afford 108 mg of **1**. Single crystals of **1** suitable for an X-ray diffraction study were obtained by slow gas-phase diffusion of heptane into a THF/2-propanol solution under CO. IR [CH$_2$Cl$_2$, cm^{-1}]: ν(CO) = 2018 w br, 1967 s br. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, –80 °C): δ = 191.4 [dt, ^1J(Rh–C) = 70.0, ^2J(P–C) = 14.5 Hz], 134.2 (2 C$_{Ph}$), 132.9 (multiplet, *ipso*-C$_{Ph}$), 131.2 (1 C$_{Ph}$), 128.7 (2 C$_{Ph}$) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ = 31.2 ppm [d, ^1J(Rh–P) = 94.4 Hz].

X-ray Structure Determinations: Data were collected with a Nonius Kappa-CCD diffractometer using monochromated Mo-K_α radiation and were measured using a combination of φ scans and ω scans with κ offsets, to fill the Ewald sphere. The data were processed by using the Denzo-SMN software package.[9] The structure was solved and refined using SHELXTL V6.1[10] for full-matrix least-squares refinement that was based on F^2. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom. Crystallographic data for the compounds is given in Table 2. Selected structural parameters are given in Table 1.

Table 2. Crystal data and structure refinement for [Rh(CO)$_2$(PPh$_3$)$_2$I] (**1**).

Empirical formula	C$_{38}$H$_{30}$IO$_2$P$_2$Rh
Formula mass	810.37
Temperature	100.0(1) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*P*21/*n*
Unit cell dimensions	a = 11.8571(2) Å, α = 90°
	b = 14.0879(2) Å, β = 97.8310(10)°
	c = 20.8420(3) Å, γ = 90°
Volume	3449.01(9) Å^3
Z	4
Density (calculated)	1.561 Mg/m^3
Absorption coefficient	1.515 mm^{-1}
F(000)	1608
Crystal size	0.20×0.17×0.07 mm
Theta range for data collection	4.14–30.03°
Index ranges	$0 \le h \le 16$, $0 \le k \le 19$, $-29 \le l \le 29$
Reflections collected	38993
Independent reflections	10020 [R(int.) = 0.068]
Completeness to θ = 30.03°	99.4%
Absorption correction	Multi-scan (Denzo-SMN)
Max. / min. transmission	0.9014 / 0.7515
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10020 / 0 / 397
Goodness-of-fit on F^2	0.891
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0376, wR_2 = 0.0658
R indices (all data)	R_1 = 0.0795, wR_2 = 0.0717
Largest diff. peak and hole	1.033 and –0.721 e·Å^{-3}

CCDC-271952 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.

Supporting Information: (see footnote on the first page of this article): 400-MHz ^{1}H NMR variable-temperature spectra of **1**.

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[1] C. Babij, D. H. Farrar, I. O. Koshevoy, A. J. Poë, S. P. Tunik, *Dalton Trans.* **2005**, 116–122.

[2] A. R. Sanger, *Can. J. Chem.* **1984**, *62*, 2168–2169.

[3] A. R. Sanger, *Can. J. Chem.* **1985**, *63*, 571–575.

[4] E. Rotondo, G. Battaglia, G. Giordano, F. P. Cusmano, *J. Organomet. Chem.* **1993**, *450*, 245–252.

[5] M. J. Payne, D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* **1997**, 3167–3175.

[6] R. H. Crabtree, *The Organometallic Chemistry of Transition Metals*, 2nd ed., John Wiley &Sons: New York, **1994**.

[7] H.-S. Lee, J.-Y. Bae, J. Ko, Y. S. Kang, H. S. Kim, S.-J. Kim, J.-H. Chung, S. O. Kang, *J. Organomet. Chem.* **2000**, *614/615*, 83–91.

[8] S. Martinengo, P. Chini, G. Giordano, *J. Organomet. Chem.* **1971**, *27*, 389–391.

[9] Z. Otwinowski, W. Minor, *Methods in Enzymology, Macromolecular Crystallography*, part A (Eds.: C. W. Carter, Jr., R. M. Sweet), Academic Press, New York, **1997**, vol. 276, pp. 307–326.

[10] G. M. Sheldrick, Bruker Analytical X-ray Systems, Bruker AXS, Inc.Madison: Wisconsin, USA, **2001**.

[11] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. J. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, in "GAUSSIAN-98", Pittsburgh, PA, Revision A.7 ed.; **1998**.

[12] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5651.

[13] W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284–298.

[14] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299–310.

[15] A. C. Marr, E. J. Ditzel, A. C. Benyei, P. Lightfoot, D. J. Cole-Hamilton, *Chem. Commun.* **1999**, 1379–1380.

[16] F. Abu-Hasanayn, T. J. Emge, J. A. Maguire, K. Krogh-Jespersen, A. S. Goldman, *Organometallics* **1994**, *13*, 5177–5180.

[17] F. M. Dixon, A. H. Eisenberg, J. R. Farrell, C. A. Mirkin, L. M. Liable-Sands, A. L. Rheingold, *Inorg. Chem.* **2000**, *39*, 3432–3433.

[18] O. V. Sizova, Y. S. Varshavskii, T. G. Cherkasova, A. B. Nikol'skii, *Russian Coord. Chem.* **2005**, *in press.*

[19] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*; 5th ed., John Wiley & Sons: New York, **1988**.

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