Polyhedron 58 (2013) 106-114

Contents lists available at SciVerse ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Isolation and X-ray structures of four Rh(PCP) complexes including a Rh(I) dioxygen complex with a short O–O bond

Yukiko Hayashi¹, David J. Szalda^{*,2}, David C. Grills, Jonathan C. Hanson, Kuo-Wei Huang³, James T. Muckerman, Etsuko Fujita^{*}

Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973-5000, United States

ARTICLE INFO

Article history: Available online 13 October 2012

Keywords: Rhodium Pincer PCP Rh–O₂ complex

ABSTRACT

The reaction of RhCl₃·H₂O with ¹Bu₂P(CH₂)₅PⁱBu₂ afforded several complexes including [Rh^{III}(H)Cl{¹Bu₂-P(CH₂)₂CH(CH₂)₂PⁱBu₂]] (**1**), [Rh^{III}HCl₂(¹Bu₂P(CH₂)₅PⁱBu₂]] (**2**), [Rh¹Cl{¹Bu₂P(CH₂)₂CH=CHCH₂PⁱBu₂]] (**3**) and [Rh¹Cl{¹Bu₂PCH₂C(O)CH=CHCH₂PⁱBu₂]] (**4**). X-ray crystal structures of **3** and **4** showed that the C=C bond on the C₅ unit of ¹Bu₂P(CH₂)₅PⁱBu₂ is bound to Rh(1) in a η^2 configuration. In **4**, the Rh atom has a trigonal pyramidal coordination geometry. The X-ray crystal structure of **2** consists of two rhodium(III) centers bridged by two ¹Bu₂P(CH₂)₅PⁱBu₂ ligands with two phosphorus atoms, one from each ligand, trans to one another. The crystal structure of the rhodium oxygen adduct with 1,3-bis(di-*t*-butyl-phosphinomethyl)benzene [RhO₂{¹Bu₂PCH₂(C₆H₃)CH₂PⁱBu₂]] (**5**) was also investigated. In this species the O₂ is η^2 coordinated to the Rh(1) center with asymmetric Rh–O bond lengths (2.087(7) and 1.998(8) Å). The O–O bond distance is short (1.337(11) Å) with v_{O-O} of 990.5 cm⁻¹. DFT calculations on complex **5** yielded two η^2 -O₂ structures that differed in energy by only 0.76 kcal/mol. The lower energy one (**5a**) had near C₂ symmetry and generally good agreement with the experimental structure. The calculated UV–Vis and IR spectra of complex **5** are in excellent agreement with experiment.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Since Moulton and Shaw reported the first examples of transition metal complexes with a new class of tridentate ligands (called PCP ligands) in 1976, [1] PCP pincer complexes (a generalized form **A** is shown in Fig. 1) have been prepared for numerous combinations of metal (M), alkyl group (R), and ligand (X) trans to the carbon ligand (X = H, halide, alkyl, etc.) [2,3]. In general, these complexes are readily prepared by cyclometallation or oxidative addition of 1,3-bis(dialkylphosphinomethyl)benzene derivatives with proper transition metal precursors. With the use of 2-methyl or ethyl-1,3-bis(dialkylphosphinomethyl)benzene, cyclometallation involving C_{aryl} – C_{alkyl} bond activation has been found to occur and has been studied extensively to get a detailed insight into the mechanism of C–C bond cleavage [4–8]. Further, PCP pincer complexes themselves have been successfully used in various reactions, e.g., dehydrogenation of alkanes [9-12], Kharasch addition reactions [13], Heck coupling reactions [14,15], O₂ activation [16,17] and even activation or reduction of CO₂ [18,19]. On the other hand, Shaw and co-workers studied metal complexation by diphosphine ligands of the type ^tBu₂P(CH₂)₂CHR(CH₂)₂P^tBu₂ (R = H, Me) with platinum group metals (Rh, Ir, Pd and Pt), and reported several PCP pincer-type complexes with ${^{t}Bu_{2}P(CH_{2})_{2}}_{2}CR$: e.g., $[RhHCl(^{t}Bu_{2}P(CH_{2})_{2}CH(CH_{2})_{2}P^{t}Bu_{2})]$ (**1** shown in Scheme 1) [20–25]. The bulky diphosphine ligand, ${}^{t}Bu_{2}P(CH_{2})_{2}CHR(CH_{2})_{2}$ P^tBu₂ stabilizes rhodium(I) complexes prepared from [RhHCl(^tBu₂-P(CH₂)₂CR(CH₂)₂P^tBu₂)] with various loosely bound gaseous molecules such as N₂, H₂, C₂H₄ and CO₂ [26,27], and a few similar complex systems including other metals or diphosphines with the -P^tBu₂ unit have also been investigated [28-32]. However, the formation of pincer-type complexes like 1 is still rare compared with formation of the PCP pincer complexes described above, and even some closely related cyclometallated species formed together with **1** in the reaction of RhCl₃·3H₂O with ${}^{t}Bu_2P(CH_2)_5P^{t}Bu_2$ have never been fully characterized [21,33]. Here, we present a detailed study of the reaction of RhCl₃·3H₂O with ^tBu₂P(CH₂)₅P^tBu₂ under several conditions modified from that reported previously [21], and the established isolation methods of several complexes (1-5) and Xray structures (2-5) including two closely related cyclometallated



^{*} Corresponding author. Tel.: +1 631 344 4356; fax: +1 631 344 5815. *E-mail address:* fujita@bnl.gov (E. Fujita).

¹ Current address: Electronics Materials Division, Electronics Department, Nagase ChemteX Corporation, 236, Tatsunocho-nakai, Tatsuno, Hyogo 679-4124, Japan.

² Research Collaborator at Brookhaven National Laboratory, Department of Natural Sciences, Baruch College, NY 10010, United States.

³ Current address: KAUST Catalysis Center, 4700 King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

^{0277-5387/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.10.006

species. The O₂ complex, **5** has an unusually short O–O bond distance (1.337(11) Å) with v_{O–O} at 990.5 cm⁻¹.

2. Experimental

2.1. Spectroscopic measurements

NMR spectra were measured on a Bruker Avance 400 MHz spectrometer. FTIR spectra were measured on a Mattson Polaris FT-IR spectrometer or a Thermo Nicolet Nexus 670 spectrometer. Mass spectra (FAB+ and ESI) were obtained at the Institute of Chemical Biology & Drug Discovery Laboratory at Stony Brook University. The compounds were analyzed by X-ray crystallography, NMR, elemental analysis and FAB-mass spectrometry.

2.2. Materials

The solvents used for reaction and recrystallization, were purified prior to use by the following procedures, and stored in an Ar-filled glovebox. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were distilled with CaH₂ and benzophenone/Na, respectively. Diethylether (Et₂O), ethanol (EtOH), 2-propanol (i-PrOH), 2-methylpridine and H₂O were degassed by freeze-thaw cycles. The deuterized solvents, CDCl₃ and d₇-DMF were degassed, and d₇-DMF was further dried over activated molecular sieves. CH₂Cl₂ and hexane were bubbled by Ar before using as eluents for column chromatography. [${}^{t}Bu_{2}PH(CH_{2})_{5}PH^{t}Bu_{2}]Br_{2}$, ${}^{t}Bu_{2}P(CH_{2})_{5}P^{t}Bu_{2}$, [RhHCl(${}^{t}Bu_{2}P(CH_{2})_{2}CH(CH_{2})_{2}P^{t}Bu_{2}$]] (1) and [RhHCl₂{ $}^{t}Bu_{2}P(CH_{2})_{5}-P^{t}Bu_{2}]_{2}$ (2) were prepared by modified methods of the procedures reported by Shaw et al., [34,21] as shown below.

2.2.1. Preparation of 1,5-bis(di-t-butylphosphonio)pentane dibromide, [^tBu₂PH(CH₂)₅PH^tBu₂]Br₂

Di-*t*-butylphosphine (4.95 g, 33 mmol) was added to a solution of 1,5-dibromopentane (3.86 g, 16 mmol) in iso-butyl methyl ketone (2.5 ml) and the mixture was heated under reflux (at 120 °C) for 7–8 h, and then cooled to ambient temperature. The white precipitate was collected by filtration and recrystallized from CH₂Cl₂/iso-butyl methyl ketone at 5 °C to give pure [^tBu₂PH(CH₂)₅PH^tBu₂]Br₂ as a white crystalline powder, (3.92 g, 47%). Since this salt is very hygroscopic, the container with this salt was stored in a glovebox. ¹H NMR (CDCl₃, rt): δ 8.17 (2H, PH, dt, ¹J(PH) = 476 Hz, ³J(H–CH₂) = 4.3 Hz), 2.49 (4H, P-CH₂, m), 2.06 (4H + 2H, -(CH₂)₃-, m), 1.56 (36H, -^tBu, d, ³J_{PH} = 16 Hz). The ¹H NMR signals assigned to PH in CDCl₃ shift remarkably depending on the concentration, while the other signals were consistent with those reported before [34].

2.2.2. Preparation of 1,5-bis(di-t-butylphosphino)pentane, ^tBu₂P(CH₂)₅P^tBu₂

A solution of 1,5-bis(di-*t*-butylphosphonio)pentane dibromide (3.90 g, 7.5 mmol) in degassed water (5 ml) was added dropwise to a solution of sodium hydroxide (2.99 g, 75 mmol) in water (10 ml) with a bottom layer of CH_2Cl_2 (20 ml). The reaction mixture was stirred vigorously for 1.5 h at room temperature and then extracted by CH_2Cl_2 . The extract was washed well with water until

the layer of water reached pH 7–7.5 and was then dried by Na₂SO₄. The crude residue after evaporation of the extract was purified by Al₂O₃ column chromatography with CH₂Cl₂ as an eluent, to give a colorless liquid as the product (1.87 g, 70%). ¹H NMR (d₇-DMF, rt): δ 1.54 (4H + 2H, –(CH₂)₃–, m), 1.40 (4H, P-CH₂, m), 1.10 (36H, –^tBu, d, ³J_{PH} = 11 Hz); ¹³P NMR (d₇-DMF, rt): δ 28.5. ¹H and ³¹P NMR spectral data for P-^tBu of this compound in CDCl₃ were consistent with those reported previously [34].

2.2.3. Preparation of the rhodium(I) olefin complex, [RhCl{^tBu₂P(CH₂)₂ CH=CHCH₂P^tBu₂]] (**3**)

A suspension of $RhCl_3 \cdot 3H_2O$ (82 mg, 0.31 mmol) with ^tBu₂P(CH₂)₅P^tBu₂ (175 mg, 0.49 mmol) in THF (4 ml)/H₂O (0.1 ml) was heated at 72-74 °C for 6 days. The reddish precipitate of 2 formed at once, completely disappeared to give 3 as the main product. After purification by a short column with Al₂O₃, an orangeyellow solid was obtained as 3 in 80% yield based on [Rh]. An orange crystalline solid was obtained by recrystallization from CH_2Cl_2 /hexane (v/v 1/3), washed by cold hexane (1 ml \times 2) and stored in an Ar-filled glovebox: FAB-mass (positive): m/z 496 (parent); Anal. Calc. For C21H44Cl1P2Rh1: C, 50.76; H, 8.93; Cl, 7.14. Found: C, 50.71; H, 9.28; Cl, 7.22%. ¹H NMR (C₆D₆, rt): δ 4.15 (1H, HC=C, m), 2.62 (2H, $-CH_2-$, m), 2.26 (1H, HC=C, m), 1.99 (2H, $-CH_2-$, m), 1.54 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH}$ = 13 Hz), 1.44 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH}$ = 12 Hz), 1.32 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH}$ = 12 Hz), 1.12 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH}$ = 13 Hz), 0.85 (2H, $-CH_2-$, m); (CDCl₃, rt): δ 4.24 (1H, HC=C, m), 2.90 (1H, -CH₂-, m), 2.50 (1H, HC=C, m), 2.27 (1H, -CH₂-, m), 2.12 (1H, -CH₂-, m), 1.63 (1H, -CH₂-, m), 1.58 (9H, -^tBu, d, ${}^{3}J_{PH} = 13 \text{ Hz}$), 1.44 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH} = 12 \text{ Hz}$), 1.33 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH} = 12 \text{ Hz}$), 1.24 (9H, $-{}^{t}Bu$, d, ${}^{3}J_{PH} = 13 \text{ Hz}$), 1.09 (2H, $-CH_{2}-$, m); ^{13}C NMR (CDCl₃, rt): δ 69.6, 36.8, 5.8, 35.1, 34.7, 33.0, 31.3, 30.0, 29.8, 29.4, 28.8, 17.4; ³¹P NMR (CDCl₃, rt): 79.5, -35.1. In the ¹H NMR spectrum of this compound in CDCl₃, the four doublets assigned to -tBu were characteristic and consistent with those reported previously [21].

2.2.4. Preparation of the dirhodium complex, ($[RhHCl_2{^tBu_2P(CH_2)_5 P^tBu_2}]_2$ (2)

A suspension of RhCl₃·3H₂O (100 mg, 0.38 mmol) with ¹Bu₂P(CH₂)₅P^tBu₂ (175 mg, 0.49 mmol) in i-PrOH (4.9 ml)/H₂O (0.1 ml) was heated at 68–70 °C for 65 h. The color of the suspension changed from chocolate-brown to brown–pink. After cooling to room temperature, the brown–pink solid was collected by filtration and washed well by Et₂O. The brown–pink solid was dried under vacuum to give **2** in 76% yield based on [Rh]. The filtrate contained complexes **1** and **3** with a ratio of 1:2. ¹H NMR (CDCl₃, rt): δ 2.55 (8H, P-CH₂, m), 1.66 (8H, –CH₂–, m), 1.50 (36H, –^tBu, t, ³J_{PH} + ⁵J_{PH} = 13 Hz), 1.44 (36H, –^tBu, d, ³J_{PH} + ⁵J_{PH} = 12 Hz), 1.22 (4H, –CH₂–, m), –31.3 (2H, Rh-H, dt, ²J_{PH} = 12 Hz, ¹J_{RhH} = 32 Hz); ³¹P NMR (CDCl₃, rt): 49.0. In the ¹H NMR spectrum of this compound in CDCl₃, the two triplets assigned to –^tBu were consistent with those reported previously [21].

2.2.5. Preparation of the cyclometallated complex, [RhHCl^tBu₂P(CH₂)₂ CH(CH)₂P^tBu₂]] (1)

A mixture of the dirhodium complex **2** (115 mg, 0.11 mmol) and 2-methylpyridine (1.4 ml) was warmed to \sim 100 °C for 30 min. The



Scheme 1. Structures of various PCP complexes.



Fig. 1. X-ray structure of $[RhHCl_2{^tBu_2P(CH_2)_5P^tBu_2}]_2$ (2).

resultant clear brownish yellow solution was cooled to room temperature and confirmed by ¹H NMR to include **1** and **3** in the ratio, ca. 4:1. Further purification of **1** was carried out using column chromatography with Al₂O₃ and then **1** was recrystallized from CH₂Cl₂/hexane. The orange crystalline solid was washed by hexane and stored under Ar: ESI mass: m/z 463.2114 (M–Cl⁻); ¹H NMR (CDCl₃, rt): δ 1.76 (4H, –CH₂–, m), 1.51 (4H, P-CH₂, m), 1.36 (36H, –^tBu, t, ³J_{PH} + ⁵J_{PH} = 13 Hz); ¹³C NMR (CDCl₃, rt): δ 49.9 (<u>C</u>CH₂CH₂P, J_{RhC} = 23 Hz), 41.9 (<u>C</u>H₂CH₂P, J_{PC} + J'_{pc} = 14 Hz), 35.4 (<u>C</u>(CH₃)₃, J_{PC} + J'_{pc} = 16 Hz), 29.1 (C(<u>C</u>H₃)₃, J_{PC} + J'_{pc} = 5 Hz), 23.6 (<u>C</u>H₂P, J_{PC} + J'_{pc} = 17 Hz); ³¹P NMR (CDCl₃, rt): 85.9.

2.2.6. Isolation of $[RhCl{^tBu_2PCH_2COCH=CHCH_2P^tBu_2}]$ (4)

During the purification of complex **1** that contains complex **3** with a long Al₂O₃ column for 1–2 h, ca. 30% of **3** decomposed to give a small amount of another rhodium(I) olefin complex, [RhCl{^tBu₂PCH₂COCH=CHCH₂P^tBu₂}] **(4)**. The rhodium(I) olefin complex, [RhCl{^tBu₂PCH₂COCH=CHCH₂P^tBu₂}] **(4)**: *Anal.* Calc. For C₂₁H₄₄Cl₁P₂Rh₁: C, 50.76; H, 8.93; Cl, 7.14. Found: C, 50.71; H, 9.28; Cl, 7.22%. ¹H NMR (CDCl₃, rt): δ 3.58 (1H, COCH=C, d, *J* = 9.5 Hz), 3.25 (1H, HC=C, m), 3.09 (1H, -CH₂-, m), 2.3–2.05 (3H, -CH₂-, m), 1.60 (9H, -^tBu, d, ³*J*_{PH} = 13 Hz), 1.46 (9H, -^tBu, d, ³*J*_{PH} = 14 Hz); 1.38 (9H, -^tBu, d, ³*J*_{PH} = 13 Hz), 1.26 (9H, -^tBu, d, ³*J*_{PH} = 14 Hz); ¹³C NMR (CDCl₃, rt): δ 208.4, 67.2, 40.5, 37.4, 35.5, 34.9, 33.7, 30.9, 30.4, 30.0, 29.8, 29.2, 27.4; ³¹P NMR (CDCl₃, rt): 13.8, -30.2.

2.2.7. Isolation of $[RhO_2\{^tBu_2PCH_2(C_6H_3)CH_2P^tBu_2\}]$ (5)

This complex was prepared by exposure of a heptane solution containing RhN₂{^tBu₂PCH₂(C₆H₃)CH₂P^tBu₂} to air. Rh(N₂){^tBu₂-PCH₂(C₆H₃)CH₂P^tBu₂} was synthesized according to literature procedures [18,26,35]. ¹H NMR (C₆D₆, rt): δ 6.96 (3H, m), 3.25 (4H, Ar-CH₂-P, t, ²J_{HP} = 3.4 Hz), 1.29 (36H, -^tBu, t, ²J_{HP} = 6.6 Hz); ³¹P NMR (C₆D₆, rt): δ 68.75 (d, ¹J_{RhP} = 146 Hz) in d⁶-benzene; IR (KBr): O–O stretching frequency 990.5 cm⁻¹ for ¹⁶O₂, 936.1 cm⁻¹ for ¹⁸O₂.

2.3. Collection and reduction of X-ray data

X-ray data sets were collected on crystals of $[RhHCl_2{^tBu_2-P(CH_2)_5P^tBu_2}]_2$ (2), $[RhCl{^tBu_2P(CH_2)_2CH=CHCH_2P^tBu_2}]$ (3), $[RhCl{^tBu_2PCH_2COCH=CHCH_2P^tBu_2}]$ (4), and $[RhO_2{^tBu_2PCH_2-(C_6H_3)CH_2P^tBu_2}]$ (5). Crystals of the complexes, 2, 3 and 4, were coated with Vaseline and sealed inside a glass capillary. Data was collected on an Eraf–Nonius CAD-4 diffractometer using Mo K α radiation (wavelength: 0.71073 Å) for 3 and Cu K α radiation

(wavelength: 1.54178 Å) for **2** and **4**. A small needle crystal of **5** ($0.125 \times 0.075 \times 0.025$ mm) was coated with "perfluoropolyether oil" and mounted on the end of an open glass capillary and data collected at beamline X4C at the National Synchrotron Light Source, Brookhaven National Laboratory (wavelength: 0.97950 Å) using the rotation method. Crystal data are provided in Table 1.

2.4. Determination and refinement of the structure

The structures were solved by standard heavy atom Patterson methods. In the least-squares refinement [36], anisotropic temperature parameters were used for all the non-hydrogen atoms. Hydrogen atoms were placed at calculated positions and allowed to ride on the atom to which they were attached. The isotropic thermal parameter for the hydrogen atoms were determined from the atom to which they were attached. A Fourier absorption correction (XABS2) [37] was used for **3**, **4** and **5**. For **2** the absorption correction was determined from the face indexing. Complex **5** is twinned by merohedry. The Flack parameter [38] is 0.44(4) indicating that the crystal is an inversion twin with approximately equal amounts of each twin component.

2.4.1. DFT calculations on $[RhO_2\{ {}^{t}Bu_2PCH_2(C_6H_3)CH_2P {}^{t}Bu_2\}]$ (5)

All calculations quoted here were carried out using density functional theory (DFT) as implemented in the GAUSSIAN 09 program package [39]. They employed the use of the B3LYP hybrid functional [40–42] and the all-electron 6-31 + G(d,p) double-zeta with polarization basis [43–48] for each atom except rhodium. For the rhodium atom the ECP28MWB + f effective core potential and basis were employed [49,50]. To investigate the possible sensitivity of the DFT-calculated structure to the choice of functional, calculations were also carried out with the M06L functional with the same basis. Further details of the calculations are provided in the SI.

3. Results and discussion

3.1. X-ray structural analysis and reactivity of $[RhHCl_2[^tBu_2P(CH_2)_5 P^tBu_2]]_2$ (2)

Crystallizations of 2 in CH₂Cl₂ at room temperature afforded deep red thin crystals suitable for single-crystal X-ray diffraction. Fig. 1 shows the structure of **2**. Crystallographic data and selected bond distances and angles are listed in Tables 1 and 2. The crystal 2 consists of two rhodium(III) bridged by two ^tBu₂P(CH₂)₅P^tBu₂ ligands with two phosphorus atoms, one from each ligand, trans to one another. The molecule crystallizes around a crystallographic center of inversion so that the asymmetry unit consists of one-half of the molecule (Fig. 1). The geometry about the rhodium(III) ion is trigonal bipyramidal. In complex 2, the equatorial sites are occupied by two chloride ions and a hydride ligand. The equatorial site is disordered with the two chlorides and the hydride disordered so that all the equatorial positions are equally occupied by chloride ligands. The hydride ligand could not be located by the X-ray analysis. The five member carbon chain of the ligand is also disordered over two positions as are some of the *t*-butyl groups. The positions of the two hydrocarbon chains could be resolved but the disordering of the *t*-butyl groups can be seen in their large thermal parameter. In 2 the Rh(III)-Cl bond distance varies between 2.300(3) to 2.338(3) while in 3 and 4 the Rh(I)-Cl bond distances are 2.377(1) and 2.360(2) Å, respectively as seen from Table 3. This decrease in bond length in 2 is consistent with the increase in oxidation state of the metal.

As reported previously [21], the ¹H and ³¹P NMR spectra of **2** showed two equivalent rhodium atoms and hydrides. In addition, Shaw et al. reported IR data of **2**: v(Rh-H) at 1941 (w), and

Table 1			
Crystallographic data	for mono-rhodium	complexes,	2, 3, 4 and 5

Complex	2	3	4	5
Formula	C ₂₁ H ₄₈ Cl ₂ P ₂ Rh	C ₂₁ H ₄₄ ClP ₂ Rh	C ₂₁ H ₄₂ ClOP ₂ Rh	C ₂₄ H ₄₃ O ₂ P ₂ Rh
Molecular weight	534.33	496.89	510.87	528.43
Crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	Pbca	P2(1)/c	C2/c	Pna2(1)
Unit cell dimensions				
a (Å)	12.458(3)	11.955(4)	23.277(5)	23.224(5)
b (Å)	15.288(3)	16.297(3)	7.446(2)	7.7450(15)
<i>c</i> (Å)	28.150(6)	13.138(4)	30.723(6)	14.006(3)
α (°)	90.00	90.00	90.00	90.00
β(°)	90.00	104.29(2)	110.05(3)	90.00
γ (°)	90.00	90.00	90.00	90.00
V (Å ³)	53561(2)	2481(1)	5002(2)	2519.3(9)
Ζ	8	4	8	4
$ ho$ (calcd) (mg m $^{-3}$)	1.3294	1.330	1.357	1.393
T (K)	293	293	293	200
Color/shape	red plate	orange-yellow prism	yellow prism	green needle
Size	$0.33\times0.33\times0.10~(mm)$	$0.50\times0.50\times0.30~(mm)$	$0.25\times0.13\times0.03~(mm)$	$0.125 \times 0.075 \times 0.025 \ (mm)$
Radiation	Cu Ka	Μο Κα	Cu Ka	0.97950 Å
μ (mm ⁻¹)	8.126	0.928	7.760	1.937
Absorption correction	integration	empirical	empirical	empirical
Number reflections collected	5496	14345	8939	1643
Number of unique reflections	5467	7230	4735	1643
Number of reflections $(I > 2\sigma (I))$	3197	3307	2436	1604
2θ limits (°)	149.5	60.0	140.2	56.2
Number of variables	271	244	235	263
$R_1^{a} (l > 2\sigma (l))$	0.0631	0.0482	0.0563	0.0425
wR_2	0.1746	0.1041	0.1268	0.1074
Maximum shift/error, final cycle	0.002	0.001	0.008	0.008

^a $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; R_w = \{ \Sigma [w(|F_0| - |F_c|^2] / \Sigma [w|F_0|^2] \}^{1/2}.$

Table 2

Selected bond lengths (Å) and angles (deg) for di-rhodium complex 2.

	$[RhHCl_{2}^{t}Bu_{2}P(CH_{2})_{5}P^{t}Bu_{2}]_{2}$ (2)
Rh(1)-Cl(1)	2.338(3)
Rh(1)-Cl(2)	2.325(3)
Rh(1)-Cl(3)	2.300(3)
Rh(1)-Cl(4)	2.316(4)
Rh(1)-P(1)	2.384(2)
Rh(1)-P(2)	2.385(2)
Cl(1)-Rh(1)-Cl(3)	167.8(2)
Cl(2)-Rh(1)-Cl(4)	167.5(2)
Cl(1)-Rh(1)-P(1)	88.9(1)
Cl(2)-Rh(1)-P(1)	88.0(1)
Cl(3)-Rh(1)-P(1)	92.4(1)
Cl(4)-Rh(1)-P(1)	91.6(1)
Cl(1)-Rh(1)-P(2)	87.3(1)
Cl(2)-Rh(1)-P(2)	88.3(1)
Cl(3)-Rh(1)-P(2)	92.0(1)
Cl(4)-Rh(1)-P(2)	92.8(1)
P(1)-Rh(1)-P(2)	175.1(1)

v(Rh-Cl) at 345 (s) cm⁻¹, and especially assigned the value of v(Rh-Cl) to a linear [Cl-Rh-Cl] unit. These are confirmed by the X-ray analysis of **2** (with an average Cl-Rh-Cl angle of 167.6(2)°). Complex **2** is reported to be converted to **1** in \ge 90% yield by heating up to 50 °C for 3 min in 2-picoline [21]. When we tried this reaction several times by using **2** that we isolated, the conversion of **2** to **1** (80%) and **3** (20%) required ~100 °C for 30 min. Addition of a few drops of H₂O to the reaction mixture gave crude **1** and **3** (5:1) in ca. 75% yield. To obtain pure **1**, column chromatography with Al₂O₃ was needed in our experiments.

3.2. X-ray structural analysis and reactivity of $[RhCl\{{}^{t}Bu_{2}P(CH_{2})_{2}CH=CHCH_{2}P^{t}Bu_{2}\}]$ (**3**) and $[RhCl\{{}^{t}Bu_{2}PCH_{2}COCH=CHCH_{2}P^{t}Bu_{2}\}]$ (**4**)

Orange–yellow crystals of **3** and yellow crystals of **4** for X-ray analysis were prepared by recrystallization from CH_2Cl_2 /hexane

at room temperature and 5 °C. Fig. 2 shows the structures of **3** and **4**, respectively and Table 3 lists selected bond distances and angles. Table 1 provides data collection and refinement details of **3** and **4**. The structure of **3** consists of a single rhodium ion coordinated to two phosphorus atoms of a single ${}^{t}Bu_2P(CH_2)_5P^{t}Bu_2$ ligand. The two carbon atoms of the olefin group in the ligand are η^2 -coordinated to the rhodium. There is also a chloride ligand in the equatorial position. The crystal itself is disordered (50–50) with the alkene bond of the five atom carbon chain being nearer to P(1) 50% of the time and nearer to P(2) the other 50%. The Rh–C bond lengths are 2.131(5) and 2.105(9) Å. The Rh–Cl bond length is 2.377(1) Å.

The structure of **4** is similar to **3** except that a ketone functional group has been incorporated into the ligand. There is no disorder in this structure and the hydrogen atoms on the alkene carbon atoms are *trans* as they are in **3**. The Rh–C distances in **3** and **4** are about the same while the Rh–P bond distances are longer in **4** than in **3** and the Rh–Cl bond distance is slightly longer in **3** than in **4** (see Table 3). Both complexes **3** and **4** have two phosphorus chemical shifts including positive and negative chemical shifts. The negative shift is characteristic of phosphorus in a four-membered ring [21]. This is consistent with the X-ray structures.

Briggs et al. found that PtCl₂(NC^tBu)₂ reacts with ^tBu₂P(CH₂)₅- $P^{t}Bu_{2}$ to give $[PtCl\{^{t}Bu_{2}P(CH_{2})_{2}CH(CH_{2})_{2}P^{t}Bu_{2}\}]$, $[PtCl\{^{t}Bu_{2}P(CH_{2})_{2} CH = CHCH_2P^tBu_2$ and other products [22]. In [PtCl{^tBu₂P(CH₂)₂CH=CHCH₂P^tBu₂}, the central carbon atom of the five-membered chain is deprotonated and coordinated to the platinum with a Pt–C bond length of 2.033(15) Å. The structure is disordered as in **3**. However, the ^tBu₂P(CH₂)₅P^tBu₂ ligand can be deprotonated with a different fashion to be a ${}^{t}Bu_{2}P(CH_{2})_{2}-C^{2-}$ -(CH₂)₂P^tBu₂ ligand (Scheme 2) [23]. The corresponding iridium complex has a structure 3b shown in Scheme 2 with a short Ir-C bond length of 2.006(4) Å. When ^tBu₂P(CH₂)₅P^tBu₂ is reacted with $RhCl_3 H_2O$, the resulting $[Rh^{III}(H)Cl\{^tBu_2P(CH_2)_2CH(CH_2)_2P^tBu_2\}]$ complex 1 is trigonal bipyramidal with a Rh-C bond length of 2.082(2) Å and a hydride ligand in the fifth coordination site [25].

Selected bond lengths (Å) and angles (deg) for mono-rhodium complexes, 3 and 4 .				
$[RhCl{tBu2P(CH2)2CH=CHCH2PtBu2}] (3)$		[RhCl{ ^t Bu ₂ PCH ₂ COCH=CHCH ₂ P ^t Bu ₂ }] (4)		
Rh(1)-C(3)	2.131(5)	2.117(8)		
Rh(1)-C(4)	2.105(9)	2.093(9)		
Rh(1)-Cl(1)	2.377(1)	2.360(2)		
Rh(1)-P(1)	2.302(1)	2.320(2)		
Rh(1)-P(2)	2.301(1)	2.322(2)		
C(4) - C(3)	1.294(12)	1.364(12)		
C(3)-Rh(1)-C(4)	35.6(3)	37.8(3)		
C(3)-Rh(1)-P(1)	87.0(2)	85.2(3)		
C(4)-Rh(1)-P(1)	100.0(4)	95.6(3)		
C(3)-Rh(1)-P(2)	86.7(2)	88.2(3)		
C(4)-Rh(1)-P(2)	69.2(4)	70.3(3)		
Cl(1)-Rh(1)-C(3)	163.7(2)	161.2(3)		
Cl(1)-Rh(1)-C(4)	157.8(3)	159.4(3)		
Cl(1)-Rh(1)-P(1)	94.3(1)	95.1(1)		
Cl(1)-Rh(1)-P(2)	94.5(1)	95.9(1)		
P(1)-Rh(1)-P(2)	168.1(1)	163.5(1)		



Fig. 2. X-ray structures of [RhCl{¹Bu₂P(CH₂)₂CH=CHCH₂P^tBu₂]] (3) and [RhCl{¹Bu₂PCH₂COCH=CHCH₂P^tBu₂]] (4).



Scheme 2. Two different coordination geometries of the deprotonated ligands from ${}^tBu_2P(CH_2)_sP{}^tBu_2.$

The Rh(III)–Cl bond length is 2.452(1)Å versus 2.377(1) and 2.360(2) in **3** and **4** for Rh(I), respectively.

In the complex formed between Rh(I) and a hexamethylene diphosphate ligand [51], the complex formed is similar to **3**, but without any disorder, with Rh-(η^2 -C=C) bond lengths of (Rh-C) 2.139(21) and 2.160(20) Å. The P-Rh-P bond angle is 176.0(2)° [51] versus 168.1(1)° in **3**. The longer carbon chain allows the P-Rh-P angle to straighten but does not affect the strength of the Rh-(η^2 -C=C) bond. The complex **3** is somewhat unstable on an Al₂O₃ column and decomposed to [RhCl{^tBu₂PCH₂COCH=CHCH₂-



Fig. 3. UV–Vis spectrum of complex 5 in *n*-heptane.

Table 3

 $P^{t}Bu_{2}$] (**4**) with ca. 15–30% yield based on [**3**]. This species was also detected when **3** was dissolved in CDCl₃ in the presence of H₂O and/or O₂ in several hours.

3.3. Structural and electronic properties of [RhO₂{^tBu₂PCH₂(C₆H₃)CH₂P^tBu₂}] (**5**)

We have recently investigated the thermodynamics and kinetics of the binding of several small molecules ($L = N_2$, H_2 , D_2 , and C₂H₄) to the photo-generated coordinatively unsaturated Rh^IPCP complexes (i.e., Rh^I{^tBu₂PCH₂(C₆H₃)CH₂P^tBu₂} and Rh^I{^tBu₂P(CH₂)₂-CH(CH₂)₂P^tBu₂}) in organic solvents (*n*-heptane, toluene, THF and cyclohexane- d_{12}) by kinetic flash photolysis methods, NMR equilibrium studies, and density functional theory (DFT) calculations [52]. When a solution containing $Rh^{I}(N_{2})$ {^tBu₂PCH₂(C₆H₃)CH₂-P^tBu₂} under 1 atm N₂ was exposed to air, the color of the solution changed from yellow to green, and the oxygen adduct was formed. The well-defined ¹H NMR suggests that this oxygen complex is diamagnetic. The UV-Vis spectrum of 5 in *n*-heptane indicates absorptions at 300, 330(sh), 470, and 662 nm (Fig. 3). The O-O stretching frequency is observed at 990.5 and 936.1 cm⁻¹ for the ¹⁶O₂ and ¹⁸O₂ adducts, respectively, in KBr disks (Figure S1 in the Supporting information). The O₂ adduct in d₆-benzene under vacuum is not stable at 25 °C and decomposes to form the free oxidized PCP ligand in 2 h.

Fine green needle crystals suitable for single crystal X-ray analysis were obtained by cooling a hexane solution of complex **5** at -80 °C. The diffraction data of **5** were collected using the National Synchrotron Light Source at BNL up to theta 28.12 degrees as a result of the experimental configuration of the beamline. This results in a structure of low precision but does not change the observation of the coordination mode of the oxygen molecule or the O–O bond distance (see Table S1 in the SI). The crystallographic data and the selected bond distances and angles are summarized in Tables 1 and 4, respectively. The η^2 coordination of the oxygen molecule in **5** can be seen in Fig. 4. The molecule has very close to mirror symmetry with the mirror plane containing O1, O2, Rh1, C31 and C34. This is in contrast to the crystallographic twofold symmetry found in



Fig. 4. X-ray structure of $[RhO_2\{^tBu_2PCH_2(C_6H_3)CH_2P^tBu_2\}]$ (5).

the closely related complex $[RhO_2\{^{t}Bu_2PCH_2(C_6H(CH_3)_2)CH_2P^{t}Bu_2\}]$ [16]. The different symmetry is a result of the two compounds being conformational isomers. In **5** the two methylene carbon atoms are both out of the best plane (0.23 and 0.25 Å) formed by the rhodium atom and the benzene ring coordinated to it while the two phosphorus atoms are on the opposite side (0.14 and 0.23 Å) of this best plane. In $[RhO_2\{^{t}Bu_2PCH_2(C_6H(CH_3)_2)CH_2P^{t}Bu_2\}]$ [16] the two methylene carbon atoms are on either side of this best plane (±0.48 Å) while the two phosphorus atoms are in this best plane (±0.004 Å). The oxygen molecule is asymmetrically coordinated to the rhodium atom with Rh–O bond distances of 2.087(7) and 1.998(8) Å. The O–O bond distance of 1.337(11) Å is short and in fact, it is shorter than that of 1.365(18) Å observed

Table 4

Selected bond lengths (Å) and angles (deg) for complex **5**, calculated η^2 -O₂ and η^1 -O₂ Complexes **5**, and related complexes.

······································						
Complex	5	Calc. $\eta^2 - O_2$, 5a	Calc. η^2 –O ₂ , 5b	Calc. $\eta^1 - O_2$	a	b
		$\begin{array}{c c} & & & P^tBu_2 \\ & & & O \\ & & & P^tBu_2 \\ & & & P^tBu_2 \end{array}$		P ^t Bu ₂ Rh _{-O} P ^t Bu ₂	$\begin{array}{c} & & & \\ & &$	$ \begin{array}{c} \begin{array}{c} P^{t}Bu_{2} \\ P^{t}Bu_{2} \\ P^{t}Bu_{2} \\ P^{t}Bu_{2} \\ H \end{array} \end{array} $
Rh(1)-O(1)	2.087(7)	2.046	2.085	2.910	2.030(8)	2.082(3)
Rh(1)-O(2)	1.998(8)	2.046	2.011	1.932		2.033(3)
Rh(1)-C(31)	2.018(11)	2.055	2.051	2.047	2.026(15)	2.195(3), 2.160(4)
Rh(1) - P(1)	2.314(2)	2.361	2.361	2.369	2.3123(16)	2.325(2)
Rh(1)-P(2)	2.324(3)	2.361	2.361	2.360		2.318(2)
O(1)-O(2)	1.337(11)	1.366	1.369	1.300	1.365(18)	1.434(4)
O(1)-Rh(1)-O(2)	38.1(3)	39.00	38.99		39.3(5)	40.8(1)
O(1)-Rh(1)-C(31)	173.4(4)	160.51	170.21	158.05	160.4(5)	179.6(1)
O(2)-Rh(1)-C(31)	148.3(4)	160.50	150.78	165.14		139.5(1)
O(1)-Rh(1)-P(1)	97.87(19)	96.52	94.76	80.78		98.2(1)
O(1)-Rh(1)-P(2)	97.7(2)	95.91	96.56	112.41		98.1(1)
O(2)-Rh(1)-P(1)	94.79(19)	95.91	96.57	101.56	96.9(2)	94.6(1)
O(2)-Rh(1)-P(2)	97.7(2)	96.53	95.33	91.74	96.3(2)	95.4(1)
C(31)-Rh(1)-P(1)	83.4(3)	83.40	83.97	83.26	82.97(7)	85.0(1)
C(31)-Rh(1)-P(2)	83.3(3)	83.40	84.04	82.98		84.9(1)
P(1)-Rh(1)-P(2)	165.99(11)	166.80	167.66	166.24	165.93(15)	162.53(8)

a denotes Ref. [16].

b denotes Ref. [56].

in the closely related complex [RhO₂{^tBu₂PCH₂(C₆H(CH₃)₂)CH₂-P^tBu₂}] [16]. It should be noted that in this complex, O₂ coordinates symmetrically to the Rh(I) center with a Rh-O bond distance of 2.030(8) Å. The difference in the coordination of the O₂ is most likely due to the difference in the conformation of the ligand. Is the asymmetric coordination of O₂ in **5** unusual? The X-ray structure of $RhH(O_2)$ {CH₂=C(CH₂CH₂P^tBu₂)₂} (see the structure in Table 4) indicates asymmetric coordination of O₂: Rh–O, 2.082(3) and 2.033(3) Å; O-O, 1.434(4) Å [26]. In this structure we find the asymmetric coordination of the O₂ molecule and the methylene groups bonded to the phosphorus atoms are both on the same side of the best plane formed by Rh1, C10, C12 and C13 (NOTE: this is not exactly like our case because C12 and C13 are also methylene groups in this case.) while the two phosphorus atoms are both on the other side of this plane as is observed in 5. The $Rh(O_2)(PNP)$ complex, $[Rh(O_2)(^tBu_2PCH_2SiMe_2)_2N]$, also shows such C_s symmetry of O_2 in two crystallographically independent molecules with short O-O bonds: Rh-O, 2.024(7) and 2.011(7) Å; O-O, 1.363(10) Å in molecule A; Rh–O, 2.019(7) and 1.998(8) Å; O–O, 1.356(11) Å in molecule B [53]. As Verat et al. wrote for the Rh(O₂)(PNP) complex, ³¹P (δ 68.75, ¹J_{RhP} 146 Hz) and ¹H NMR (δ 3.23, vt, 4H, ${}^{3}I_{HP}$ = 3.2 Hz, Ar–CH₂–P)) spectra of complex 5 in d₆benzene are consistent with a C_{2v} structure, however, it is quite possible that the C_s structure is fluxional to show time-averaged C_{2v} symmetry. It should be noted that recent X-ray structures of N-heterocyclic carbene complexes of Rh(I) dioxygen adducts also show extremely short O-O bond distances considering it is 1.21 Å for free O_2 : ClRh(IMes)₂(O_2) where IMes = 1,3-dimesitylimidazol-2-ylidene [54], 1.267(13) and 1.271(14) Å; $ClRh(IPr)_2(O_2)$ where IPr = N, N-bis(2,6-diisopropylphenyl)imidazol)-2-ylidene [54], 1.315(3) Å).

In **5**, O(1) and O(2) are 0.114 and 1.156 Å above and below, respectively, the best plane formed by Rh(1), P(1), P(2) and C(31). In the closely related complex [RhO₂{^tBu₂PCH₂(C₆H(CH₃)₂)CH₂-P^tBu₂}] in which the oxygen molecule is symmetrically coordinated as mentioned above, each oxygen atom lies ± 0.68 Å above or below the best plane formed by Rh, P, P, and C [16]. The coordination of the oxygen molecule in **5** is more similar to that which was observed in [RhHO₂{CH₂=C(CH₂CH₂P^tBu₂]] in which the oxygen atoms of the coordinated oxygen molecule are 0.35 and 1.67 Å above the best plane formed by Rh, P, P, and C [26]. Distances of the carbon atoms of the C=C bonds from best planes for complexes **3** and **4** are listed in Table S2.

In order to understand the short O-O bond distance and the asymmetric nature of O_2 coordination to the Rh(I) center in 5, we calculated the optimized structures of the η^2 -O₂ and η^1 -O₂ species (see Figure S2 in the Supporting information). Because the NMR of species 5 indicated that it was diamagnetic, we considered only closed-shell singlet structures. We found two local minima corresponding to structural conformers of the η^2 -O₂ species. The structure with the lower energy (by 0.76 kcal/mol), **5a**, had near C_2 symmetry, essentially equal Rh-O bond lengths, and general agreement with the structure reported by Milstein [16]. The other conformer, **5b**, had near C_s symmetry, unequal Rh–O bond lengths and general agreement with the structure of **5** reported here. The near C_2 symmetry structure was also calculated using the M06L functional, which yielded a structure very similar to that with the B3LYP functional (see Table S3 in the SI), to investigate the effect of the choice of functional on the structure. Table 4 compares the calculated bond distances and angles of the η^2 -O₂ **5a** and **5b** structures, as well as the η^1 –O₂ structure, with the X-ray data from **5**. The calculated bond distances are generally about 0.03 Å longer than the experimental ones. As mentioned above, the calculated structure **5b** exhibits the best agreement with the experimental data. The difference in orientation of the bound O₂ in the complex also affects the O-Rh-C(31) bond angles substantially.

Cramer et al. [55] have suggested that libration of the O_2 moiety could lead to an underestimation of the O–O bond length. While there appears to be some evidence for it in the shape of the ellipsoids from the X-ray structure refinement, we cannot verify this effect. The discrepancy between the magnitude of the asymmetry in calculated and experimental Rh–O bond lengths might also be accentuated by the same O_2 libration.

The sterically hindered binding site at the Rh center raised the question of whether an O₂ molecule approaching the (PCP)Rh species in an end-on (i.e., η^1 –O₂) manner would smoothly form the η^2 complex or become temporarily trapped in a metastable η^1 –O₂ complex. The η^1 –O₂ and η^2 –O₂ complexes have all real vibrational frequencies; the free energy of the η^2 –O₂ complex **5a**



Fig. 5. TD-DFT calculated UV-Vis spectra of η^2 -O₂ **5a** (top) and **5b** (middle) and η^1 -O₂ (bottom) complexes of **5**.

is 13.65 kcal/mol lower. Calculated vibrational frequencies for the **5a** complex are: O–O stretching 1074 cm⁻¹, Rh–O₂ asymmetric stretch 534 cm⁻¹, and Rh–O₂ symmetric stretch 446 cm⁻¹. Assuming the scale factor of 0.9614 for B3LYP @ 6-31G(d,p), O–O stretching becomes 1033 cm⁻¹. The bond distances and angles of the η^1 complex are also listed in Table 4. Calculated vibrational frequencies for the **5b** η^2 –O₂ complex are: O–O stretching 1065 cm⁻¹, Rh–O₂ asymmetric stretch 541 cm⁻¹, and Rh–O₂ symmetric stretch 435 cm⁻¹. Assuming the scale factor of 0.9614, O–O stretching becomes 1024 cm⁻¹, which is close to the experimental value of 990.5 cm⁻¹.

The UV–Vis spectra of the η^2 –O₂ complexes **5a** and **5b** (Fig. 5, top two panels), calculated using TD–DFT with GAUSSIAN broadening of the discrete transitions with a 0.18 eV half-width are both in excellent agreement with the experimental spectrum in Fig. 3. The nearly universal acceptor orbital in all the transitions indicated by the "stick spectrum" is orbital 126 (LUMO), which is largely Rh–O σ^* in character but also has phenyl π^* character. Not shown in the figure is a weak HOMO \rightarrow LUMO transition at 1315 nm. The weak band at 694 nm is primarily orbital 124 Rh(d) \rightarrow LUMO, and that at 444 nm corresponds to orbitals (120 Rh–O π , phenyl π^*) and 121 (Rh–O " δ ", phenyl π^*) \rightarrow LUMO. The remaining transitions in the visible (down to 323 nm) are weak metal-to-ligand charge transfer transitions.

The calculated spectrum of the η^1 –O₂ complex (Fig. 5, bottom panel) is strikingly different, especially in the intensity of the band at ca. 430 nm. Again, there is a very weak HOMO \rightarrow LUMO transition (not shown) at 3532 nm, and a peak similar to that in the



Fig. 6. Selected frontier orbitals of (PCP)Rh(η^2 –O₂) **5b.** Orbital 121 is analogous to the " δ " bonding orbital between a d_{π} Rh orbital and the "out-of-plane" π^* orbital of O₂ described by Ref. [55]; orbital 125 (HOMO) is the corresponding δ^* orbital. Orbital 122 is analogous to the interaction between an 'in-plane" d_{π} orbital of Rh and the "in-plane" π^* orbital of O₂ also described by Ref. [55] that decreases the O₂ bond order while increasing the Rh–O bond order. Orbital 126 (LUMO) is the nearly universal acceptor of photoexcited electrons in the visible region of the molecular spectrum, and is largely a Rh–O σ^* orbital.

 η^2 –O₂ complex at 680 nm. The increased intensity in the transitions at 453, 438 and 427 nm in the η^1 –O₂ complex arises from the character of the donor orbitals, which are Rh–phenyl π , Rh–O π or phenyl π^* in character. The acceptor orbital in all cases is the LUMO which is Rh–O π^* , O–O π^* and phenyl π^* in character.

The bonding of the O₂ to Rh in the **5a** and **5b** complexes is more complicated than might be expected. The d⁸ Rh(I) center in pseudo square planar complexes (with the z-axis perpendicular to the P-C-P-Rh plane) has pairs of electrons in the lowest (degenerate) d_{vz} and $d_{xz}(d_{\pi})$ orbitals, another pair in the d_{z^2} orbital, and still another pair in the d_{xy} orbital, with the highest lying $d_{x^2-y^2}$ orbital unoccupied. Orbital 121 is a " δ -like" bonding orbital formed from the overlap of the out-of-plane d_{π} orbital of Rh with the out-of-plane π^* orbital of O₂ as described by Cramer et al. [54]. Orbital 125 (HOMO) is the corresponding " δ^* " orbital. Orbital 122 results from the interaction between the in-plane d_{π} orbital of Rh and the inplane π^* orbital of O₂, also described by Cramer et al. [54] that decreases the O₂ bond order while increasing the Rh–O bond order. Orbital 126 (LUMO) is the corresponding (unoccupied) antibonding Rh-O orbital which is the nearly universal acceptor of photoexcited electrons throughout the visible region of the molecular spectrum. These orbitals are shown for 5b in Fig. 6 and for 5a in Fig. S3 (see SI). Comparison of these similar orbitals for structures **5a** and **5b** clearly reflects the near C_2 versus near C_s symmetry of the two complexes.

4. Conclusions

Through a detailed separation of the products in the reaction of RhCl₃·3H₂O with ^tBu₂P(CH₂)₅P^tBu₂, we have isolated two novel types of Rh(I)-olefin complexes, [RhCl{Bu₂P(CH₂)₂CH=CHCH₂- $P^{t}Bu_{2}$] (**3**), and [RhCl{^tBu₂PCH₂COCH=CHCH₂P^tBu₂}] (**4**) in addition to $[Rh^{III}(H)Cl\{^{t}Bu_{2}P(CH_{2})_{2}CH(CH_{2})_{2}P^{t}Bu_{2}\}]$ (1) and the dinuclear Rh complex $[Rh^{III}HCl_2[^tBu_2P(CH_2)_5P^tBu_2]]_2$ (2). Complex **4** is produced *via* decomposition of **3** on an Al₂O₃ column or the slow reaction of **3** with H_2O (or O_2) in solution at room temperature. In their X-ray structures, the coordination of C=C to Rh is η^2 binding similar to Cl-Pt{Bu^t₂P(CH₂)₂C=CHCH₂PBu^t₂} complexes. Complex **5** contains an η^2 -coordinated oxygen with asymmetric Rh-O bond lengths and a short O-O bond of 1.337(11) Å. DFT calculations on complex **5** yielded two η^2 –O₂ structures that differed in energy by only 0.76 kcal/mol. The lower energy one (5a) had near C₂ symmetry, and had nearly equal Rh–O bond lengths, while the higher energy structure (**5b**) had near C_s symmetry and generally good agreement with the experimental structure. The calculated UV-Vis spectra of both complex 5a and 5b are in excellent agreement with experiment. The calculations also predict a metastable η^1 –O₂ singlet complex with energy 13.65 kcal/mol higher than the η^2 –O₂ **5a** complex, and has a much stronger absorption at ca. 430 nm than either of the η^2 -O₂ complexes.

Acknowledgements

This work performed at Brookhaven National Laboratory was carried out under contract DE-AC02-98CH10886 with the US Department of Energy and supported by its Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences. Use of the National Synchrotron Light Source beamline X4C at Brookhaven National Laboratory was supported by the Scientific User Facilities Division, Office of Basic Energy Sciences.

Appendix A. Supplementary data

CCDC 889632 (**2**), 889630 (**3**), 889631 (**4**), and 889633 (**5**) contains the supplementary crystallographic data for this paper. 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 The following supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.poly.2012.10.006.

O–O stretching frequencies of complex 5 with O₂ isotope labeling in KBr disks, calculated structures of η^2 -O₂ complexes (**5a** and **5b**) and η^1 -O₂ complex **5**, selected frontier orbitals of (PCP)Rh(η^2 - O_2) **5a**, distance from best planes, selected bond lengths (Å), and angles and dihedral angles (deg) for η^2 -O₂ complex **5a** calculated with B3LYP and M06L density functional, and calculated Cartesian coordinates of η^2 -O₂ complexes (**5a** and **5b**) and η^1 -O₂ complex **5**.

References

- [1] C.J. Moulton, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020.
- [2] M. Albrecht, G. van Koten, Angew, Chem., Int. Ed. 40 (2001) 3750. [3] G.v. Koten, Pure Appl. Chem. 61 (1989) 1681.
- [4] S.Y. Liou, M. Gozin, D. Milstein, J. Am. Chem. Soc. 117 (1995) 9774. [5] B. Rybtchinski, D. Milstein, J. Am. Chem. Soc. 121 (1999) 4528.
- [6] M.E. van der Boom, S.Y. Liou, Y. Ben-David, M. Gozin, D. Milstein, J. Am. Chem. Soc. 120 (1998) 13415.
- [7] M.E. van der Boom, Y. Ben-David, D. Milstein, Chem. Commun. (1998) 917.
- [8] M. Gandelman, A. Vigalok, L. Konstantinovski, D. Milstein, J. Am. Chem. Soc. 122 (2000) 9848
- [9] M. Kanzelberger, B. Singh, M. Czerw, K. Krogh-Jespersen, A.S. Goldman, J. Am. Chem. Soc. 122 (2000) 11017.
- [10] M. Gupta, C. Hagen, W.C. Kaska, R.E. Cramer, C.M. Jensen, J. Am. Chem. Soc. 119 (1997) 840.
- [11] F.C. Liu, E.B. Pak, B. Singh, C.M. Jensen, A.S. Goldman, J. Am. Chem. Soc. 121 (1999) 4086.
- [12] F. Gorla, A. Togni, L.M. Venanzi, A. Albinati, F. Lianza, Organometallics 13 (1994) 1607
- [13] R.A. Gossage, L.A. Van De Kuil, G. Van Koten, Acc. Chem. Res. 31 (1998) 423.
- [14] M. Ohff, A. Ohff, M.E. vanderBoom, D. Milstein, J. Am. Chem. Soc. 119 (1997) 11687
- [15] D. Morales-Morales, R. Redon, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619
- [16] C.M. Frech, L.J.W. Shimon, D. Milstein, Helv. Chim. Acta 89 (2006) 1730.
- [17] D.B. Williams, W. Kaminsky, J.M. Mayer, K.I. Goldberg, Chem. Commun. (2008) 4195
- [18] W.C. Kaska, S. Nemeh, A. Shirazi, S. Potuznik, Organometallics 7 (1988) 13.
- [19] D.W. Lee, C.M. Jensen, D. Morales-Morales, Organometallics 22 (2003) 4744.
- [20] N.A. Alsalem, H.D. Empsall, R. Markham, B.L. Shaw, B. Weeks, J. Chem. Soc., Dalton Trans. (1979) 1972.
- [21] C. Crocker, R.J. Errington, R. Markham, C.J. Moulton, K.J. Odell, B.L. Shaw, J. Am. Chem. Soc. 102 (1980) 4373.

- [22] J.R. Briggs, A.G. Constable, W.S. McDonald, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1982) 1225
- [23] C. Crocker, H.D. Empsall, R.J. Errington, E.M. Hyde, W.S. McDonald, R. Markham, M.C. Norton, B.L. Shaw, B. Weeks, J. Chem. Soc., Dalton Trans. (1982) 1217.
- [24] R.J. Errington, W.S. McDonald, B.L. Shaw, J. Chem. Soc., Dalton Trans. (1982) 1829.
- [25] C. Crocker, R.J. Errington, W.S. McDonald, K.J. Odell, B.L. Shaw, R.J. Goodfellow, J. Chem. Soc., Chem. Commun. (1979) 498.
- [26] A. Vigalok, Y. BenDavid, D. Milstein, Organometallics 15 (1996) 1839.
- [27] A. Vigalok, H.B. Kraatz, L. Konstantinovsky, D. Milstein, Chem. Euro. J. 3 (1997) 253.
- [28] M.A. McLouglin, N.L. Keder, W.T.A. Harrison, R.J. Flesher, H.A. Mayer, W.C. Kaska, Inorg. Chem. 38 (1999) 3223.
- [29] A.L. Seligson, W.C. Trogler, Organometallics 12 (1993) 738.
- [30] S. Sjovall, O.F. Wendt, C. Andersson, J. Chem. Soc., Dalton Trans. (2002) 1396.
- [31] D.G. Gusev, A.J. Lough, Organometallics 21 (2002) 5091.
- [32] M.E. van der Boom, D. Milstein, Chem. Rev. 103 (2003) 1759
- [33] A. Vigalok, D. Milstein, Organometallics 19 (2000) 2061.
- [34] N.A. Al-Salem, H.D. Empsall, R. Markham, B.L. Shaw, B. Weeks, J. Chem. Soc., Dalton Trans. (1979) 1972.
- [35] S. Nemeh, C. Jensen, E. Binamirasoriaga, W.C. Kaska, Organometallics 2 (1983) 1442.
- Sheldrick, G. M., S.V.S.A.I., Inc., Madison, WI, 1994. [36]
- S. Parkins, B. Moezzi, H. Hope, J. Appl. Crystallogr. 28 (1995) 53. [37]
- [38] H.D. Flack, Acta Cryst. A39 (1983) 876.
- [39] Frisch, M.J.T., et al., GAUSSIAN, Inc., Wallingford, CT, 2009.
- [40] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
- [41] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [42] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [43] R. Ditchfield, W.J. Hehre, J.A. Pople, J. Chem. Phys. 54 (1971) 724.
- [44] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
- [45] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
- [46] P.C. Hariharan, J.A. Pople, Mol. Phys. 27 (1974) 209.
- [47] M.S. Gordon, Chem. Phys. Lett. 76 (1980) 163.
- [48] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. Defrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.
- [49] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, Theor. Chim. Acta 77 (1990) 123.
- [50] J.M.L. Martin, A. Sundermann, J. Chem. Phys. 114 (2001) 3408.
- [51] R. Mason, G.R. Scollary, Aust. J. Chem. 31 (1978) 781.
- [52] M.D. Doherty, D.C. Grills, K.-W. Huang, J.T. Muckerman, D.E. Polyansky, R.V. Eldik, E. Fujita, Inorg. Chem. Submitted.
- [53] A.Y. Verat, H.J. Fan, M. Pink, Y.S. Chen, K.G. Caulton, Chem. Eur. J. 14 (2008) 7680
- [54] J.M. Praetorius, D.P. Allen, R.Y. Wang, J.D. Webb, F. Grein, P. Kennepohl, C.M. Crudden, J. Am. Chem. Soc. 130 (2008) 3724.
- [55] C.J. Cramer, W.B. Tolman, K.H. Theopold, A.L. Rheingold, Proc. Natl. Acad. Sci. U.S.A 100 (2003) 3635.
- [56] A. Vigalok, L.J.W. Shimon, D. Milstein, Chem. Commun. (1996) 1696.