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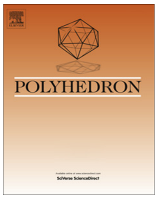

Isolation and X-ray structures of four Rh(PCP) complexes including a Rh(I) dioxygen complex with a short O–O bond

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ABSTRACT

The reaction of $RhCl_3 \cdot H_2O$ with $^tBu_2P(CH_2)_5P^tBu_2$ afforded several complexes including $[Rh^{III}(H)Cl\{^tBu_2P(CH_2)_2CH(CH_2)_2P^tBu_2\}]$ (**1**), $[Rh^{III}HCl_2\{^tBu_2P(CH_2)_5P^tBu_2\}]_2$ (**2**), $[Rh^{I}Cl\{^tBu_2P(CH_2)_2CH{=}CHCH_2P^tBu_2\}]$ (**3**) and $[Rh^{I}Cl\{^tBu_2PCH_2C(O)CH{=}CHCH_2P^tBu_2\}]$ (**4**). X-ray crystal structures of **3** and **4** showed that the C=C bond on the C_5 unit of $^tBu_2P(CH_2)_5P^tBu_2$ is bound to Rh(I) 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 $^tBu_2P(CH_2)_5P^tBu_2$ 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*-butylphosphinomethyl)benzene $[RhO_2\{^tBu_2PCH_2(C_6H_3)CH_2P^tBu_2\}]$ (**5**) was also investigated. In this species the O_2 is η^2 coordinated to the Rh(I) 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 ν_{O-O} of 990.5 cm^{-1}. DFT calculations on complex **5** yielded two η^2–O_2 structures that differed in energy by only 0.76 kcal/mol. The lower energy one (**5a**) had near C_2 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 and IR spectra of complex **5** are in excellent agreement with experiment.

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], O_2 activation [16,17] and even activation or reduction of CO_2 [18,19]. On the other hand, Shaw and co-workers studied metal complexation by diphosphine ligands of the type $^tBu_2P(CH_2)_2CHR(CH_2)_2P^tBu_2$ (R = H, Me) with platinum group metals (Rh, Ir, Pd and Pt), and reported several PCP pincer-type complexes with $\{^tBu_2P(CH_2)_2\}_2CR$: e.g., $[RhHCl(^tBu_2P(CH_2)_2CH(CH_2)_2P^tBu_2)]$ (**1** shown in Scheme 1) [20–25]. The bulky diphosphine ligand, $^tBu_2P(CH_2)_2CHR(CH_2)_2P^tBu_2$ stabilizes rhodium(I) complexes prepared from $[RhHCl(^tBu_2P(CH_2)_2CR(CH_2)_2P^tBu_2)]$ with various loosely bound gaseous molecules such as N_2, H_2, C_2H_4 and CO_2 [26,27], and a few similar complex systems including other metals or diphosphines with the $-P^tBu_2$ 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 $RhCl_3 \cdot 3H_2O$ with $^tBu_2P(CH_2)_5P^tBu_2$ have never been fully characterized [21,33]. Here, we present a detailed study of the reaction of $RhCl_3 \cdot 3H_2O$ with $^tBu_2P(CH_2)_5P^tBu_2$ under several conditions modified from that reported previously [21], and the established isolation methods of several complexes (**1**–**5**) and X-ray structures (**2**–**5**) including two closely related cyclometallated

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species. The O_2 complex, **5** has an unusually short O–O bond distance (1.337(11) Å) with ν_{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 CaH_2 and benzophenone/Na, respectively. Diethylether (Et_2O), ethanol (EtOH), 2-propanol (i-PrOH), 2-methylpridine and H_2O were degassed by freeze–thaw cycles. The deuterized solvents, $CDCl_3$ and d_7-DMF were degassed, and d_7-DMF was further dried over activated molecular sieves. CH_2Cl_2 and hexane were bubbled by Ar before using as eluents for column chromatography. [$^tBu_2PH(CH_2)_5PH^tBu_2$]Br_2, $^tBu_2P(CH_2)_5P^tBu_2$, [$RhHCl(^tBu_2P(CH_2)_2CH(CH_2)_2P^tBu_2)$] (**1**) and [$RhHCl_2\{^tBu_2P(CH_2)_5P^tBu_2\}]_2$ (**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, [$^tBu_2PH(CH_2)_5PH^tBu_2$]Br_2

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 CH_2Cl_2/iso-butyl methyl ketone at 5 °C to give pure [$^tBu_2PH(CH_2)_5PH^tBu_2$]Br_2 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. ^{1}H NMR ($CDCl_3$, rt): δ 8.17 (2H, PH, dt, ^{1}J(PH) = 476 Hz, ^{3}J(H–CH_2) = 4.3 Hz), 2.49 (4H, P-CH_2, m), 2.06 (4H + 2H, –$(CH_2)_3$–, m), 1.56 (36H, –^{t}Bu, d, $^3J_{PH}$ = 16 Hz). The ^{1}H NMR signals assigned to PH in $CDCl_3$ 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, $^tBu_2P(CH_2)_5P^tBu_2$

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 Na_2SO_4. The crude residue after evaporation of the extract was purified by Al_2O_3 column chromatography with CH_2Cl_2 as an eluent, to give a colorless liquid as the product (1.87 g, 70%). ^{1}H NMR (d_7-DMF, rt): δ 1.54 (4H + 2H, –$(CH_2)_3$–, m), 1.40 (4H, P-CH_2, m), 1.10 (36H, –^{t}Bu, d, $^3J_{PH}$ = 11 Hz); ^{13}P NMR (d_7-DMF, rt): δ 28.5. ^{1}H and ^{31}P NMR spectral data for P-^{t}Bu of this compound in $CDCl_3$ were consistent with those reported previously [34].

2.2.3. Preparation of the rhodium(I) olefin complex, [$RhCl\{^tBu_2P(CH_2)_2CH{=}CHCH_2P^tBu_2\}$] (**3**)

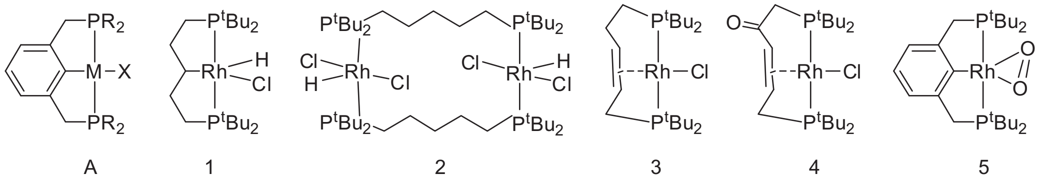
A suspension of $RhCl_3\cdot3H_2O$ (82 mg, 0.31 mmol) with $^tBu_2P(CH_2)_5P^tBu_2$ (175 mg, 0.49 mmol) in THF (4 ml)/H_2O (0.1 ml) was heated at 72–74 °C for 6 days. The reddish precipitate of **2** formed at once, completely disappeared to give **3** as the main product. After purification by a short column with Al_2O_3, an orange–yellow 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 × 2) and stored in an Ar-filled glovebox: FAB-mass (positive): *m/z* 496 (parent); *Anal.* Calc. For $C_{21}H_{44}Cl_1P_2Rh_1$: C, 50.76; H, 8.93; Cl, 7.14. Found: C, 50.71; H, 9.28; Cl, 7.22%. ^{1}H NMR (C_6D_6, 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, $^3J_{PH}$ = 13 Hz), 1.44 (9H, –^{t}Bu, d, $^3J_{PH}$ = 12 Hz), 1.32 (9H, –^{t}Bu, d, $^3J_{PH}$ = 12 Hz), 1.12 (9H, –^{t}Bu, d, $^3J_{PH}$ = 13 Hz), 0.85 (2H, –CH_2–, m); ($CDCl_3$, rt): δ 4.24 (1H, HC=C, m), 2.90 (1H, –CH_2–, m), 2.50 (1H, HC=C, m), 2.27 (1H, –CH_2–, m), 2.12 (1H, –CH_2–, m), 1.63 (1H, –CH_2–, m), 1.58 (9H, –^{t}Bu, d, $^3J_{PH}$ = 13 Hz), 1.44 (9H, –^{t}Bu, d, $^3J_{PH}$ = 12 Hz), 1.33 (9H, –^{t}Bu, d, $^3J_{PH}$ = 12 Hz), 1.24 (9H, –^{t}Bu, d, $^3J_{PH}$ = 13 Hz), 1.09 (2H, –CH_2–, m); ^{13}C NMR ($CDCl_3$, 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; ^{31}P NMR ($CDCl_3$, rt): 79.5, −35.1. In the ^{1}H NMR spectrum of this compound in $CDCl_3$, the four doublets assigned to –^{t}Bu were characteristic and consistent with those reported previously [21].

2.2.4. Preparation of the dirhodium complex, ([$RhHCl_2\{^tBu_2P(CH_2)_5P^tBu_2\}]_2$ (**2**)

A suspension of $RhCl_3\cdot3H_2O$ (100 mg, 0.38 mmol) with $^tBu_2P(CH_2)_5P^tBu_2$ (175 mg, 0.49 mmol) in i-PrOH (4.9 ml)/H_2O (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 Et_2O. 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. ^{1}H NMR ($CDCl_3$, rt): δ 2.55 (8H, P-CH_2, m), 1.66 (8H, –CH_2–, m), 1.50 (36H, –^{t}Bu, t, $^3J_{PH}$ + $^5J_{PH}$ = 13 Hz), 1.44 (36H, –^{t}Bu, d, $^3J_{PH}$ + $^5J_{PH}$ = 12 Hz), 1.22 (4H, –CH_2–, m), −31.3 (2H, Rh-H, dt, $^2J_{PH}$ = 12 Hz, $^1J_{RhH}$ = 32 Hz); ^{31}P NMR ($CDCl_3$, rt): 49.0. In the ^{1}H NMR spectrum of this compound in $CDCl_3$, the two triplets assigned to –^{t}Bu were consistent with those reported previously [21].

2.2.5. Preparation of the cyclometallated complex, [$RhHCl\{^tBu_2P(CH_2)_2CH(CH)_2P^tBu_2\}$] (**1**)

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



Scheme 1. Structures of various PCP complexes.