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Photocatalytic properties of new cyclopentadienyl and indenyl rhodium(I) carbonyl complexes with water-soluble 1,3,5-triaza-7-phosphaadamantane (PTA) and tris(2-cyanoethyl)phosphine

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ABSTRACT

Reactions of $[(\eta^5\text{-R})Rh(CO)_2]$ (R = cp, ind) with water-soluble phosphines (L = 1,3,5-triaza-7-phosphaadamantane and tris(2-cyanoethyl)phosphine) give the new rhodium(I) complexes of the types $[Rh(\eta^5\text{-cp})(CO)(PTA)]$ (**1**), $[Rh(\eta^5\text{-cp})(CO)(P(CH_2CH_2CN)_3)]$ (**2**), $[Rh(\eta^5\text{-ind})(CO)(PTA)]$ (**3**) and $[Rh(\eta^5\text{-ind})(CO)(P(CH_2CH_2CN)_3)]$ (**4**) in isolated yields of 52–75%. All these compounds have been fully characterized by IR, ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR, FAB-MS spectroscopies and elemental analyses. Reactivity for the substitution of phosphine is greater for $[(\eta^5\text{-ind})Rh(CO)(L)]$ comparing to $[(\eta^5\text{-cp})Rh(CO)(L)]$ because of a flexibility of the indenyl ligand to undergo facile η^5–η^3 coordinative isomerizations. The obtained complexes are active catalyst precursors for the dehydrogenation of propan-2-ol, octane and cyclooctane under photoassisted conditions without any organic hydrogen transfer acceptors, giving TOFs of 26–56 using **3** as precatalyst.

1. Introduction

Rhodium complexes containing indenyl (ind) and cyclopentadienyl (cp) ligands have been extensively studied, particularly those of formula $[(\eta^5\text{-R})Rh(L)_2]$ (R = cp, ind; L = phosphine, alkene, CO) [1], which participate in numerous transformations crossing from hydrosilylation [2] to C–H bond activation and functionalization of organic compounds [3]. Transition metal indenyl complexes display enhanced reactivity in both stoichiometric and catalytic reactions, compared to their cyclopentadienyl analogues [4]. The reason for this higher reactivity, which is commonly referred to as indenyl effect, is generally attributed to a re-aromatization of the fused arene ring in the transition state (Scheme 1) [4].

Special attention was devoted to studies on the photochemical activation of $[(\eta^5\text{-R})Rh(L)_2]$ to generate an unsaturated species capable of activation of C–H bonds [3a,5], but there were also other applications in catalysis [6]. It has been shown that the thermodynamically unfavourable reactions, like those of alkane dehydrogenation, may be enhanced by hydrogen transfer from alkane to sacrificial hydrogen acceptors, by thermal hydrogen evolution at high temperature, or more effectively, by photoirradiation under mild conditions [7]. Selective synthesis of functional products directly from alkanes remains a prominent challenge in research because saturated hydrocarbons are abundant and still comparatively inexpensive chemical feedstocks [8]. The photochemical conversions of alkanes to aldehydes [9], as well as dehydrogenation of alkanes and alcohols [10], catalyzed by Vaska-type rhodium complexes $[RhCl(CO)(PR_3)_2]$ were reported previously. In these complexes, trimethylphosphine (PMe_3) was used as the ligand that allows to achieve good selectivity and a high yield in catalytic reactions. However, these studies were carried out only in non-aqueous solvents for stability reasons.

Increasing interest in the reactions of transition-metal organometallic complexes in water is due to the possible availability of new reaction modes and the environmentally benign nature of the solvent. Therefore, the air-stable tertiary phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) can be used as a water-soluble analogue of PMe_3, taking into account its small size (cone angle = 103°) and electronic properties [11,12].

The coordination chemistry of PTA has experienced in the last years a rapid development mainly justified by the search for water-soluble transition-metal phosphine complexes [11]. They usually show a good solubility in aqueous media, finding therefore several applications either as catalysts in aqueous phase [11,13], water-

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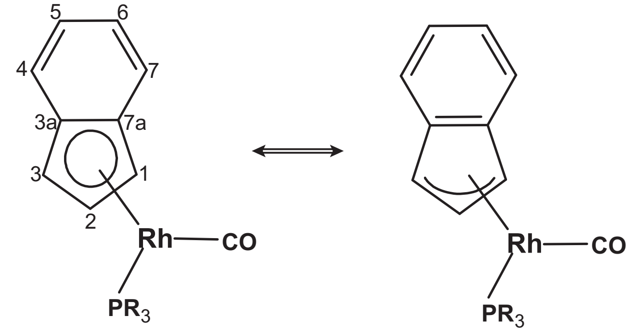


Scheme 1. Two of the possible bonding modes ($\eta^5 \leftrightarrow \eta^3$) in indenyl metal complexes with numbering scheme for the indenyl group.

soluble antitumour and antimicrobial agents [11,14] or photoluminescent materials [11,15]. Concerning the catalytic properties, in particular, it has been shown that Rh and Ru complexes with PTA and *N*-alkylated PTA can act as efficient catalysts for hydrogenation, hydroformylation and isomerization of alkenes in aqueous systems [12,16]. Moreover, anticancer properties of arene complexes with PTA [11], such as [Rh(η^5-C_5H_5)(PTA)$_2$] and [Rh(η^5-C_5Me_5)(CO)(PTA)] [17], were also reported.

In this contribution we report the synthesis and photocatalytic properties of new water soluble and water stable rhodium(I) complexes bearing aminophosphine PTA, with general formulae [Rh(η^5-R)(CO)(PTA)] (R = cp, ind). Reactivity and catalytic properties of these compounds were compared to analogous, new complexes with tris(2-cyanoethyl)phosphine, having slightly different steric and electronic properties. All compounds have been characterized by IR, ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} and FAB-MS spectroscopies and elemental analyses. They were tested as homogeneous precursors for the catalytic photoassisted dehydrogenation of hydrocarbons and propan-2-ol under mild conditions.

2. Experimental

2.1. General

All syntheses were performed under an inert atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were dried and distilled prior to use. [{Rh(CO)$_2$(μ-Cl)}$_2$], [{Rh(C_2H_4)$_2$(μ-Cl)}$_2$], organic substrates for catalysis, standards for GC (Aldrich) and tris(2-cyanoethyl)phosphine (Stream) were used as received, while 1,3,5-triaza-7-phosphaadamantane (PTA) [18], [Rh(η^5-cp)(CO)$_2$] [19] and [Rh(η^5-ind)(CO)$_2$]$_2$ [20] were synthesized in accordance with modified literature methods. Elemental analyses were performed on a Vario EL III apparatus. Infrared spectra (4000–400 cm^{-1}) were recorded with a Bruker IFS 1113v instrument in KBr pellets. NMR spectra were measured using a Bruker 300 AMX spectrometer. Mass spectra were recorded on a Varian MAT 311A (70 eV) [Institute of Inorganic and Analytical Chemistry, Technical University of Berlin, Germany]. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to Si(Me)$_4$, and δ(^{31}P) relative to 85% H_3PO_4. Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet.

The photocatalytic dehydrogenation of propan-2-ol, octane and cyclooctane were carried out in a closed system in an externally photoirradiated apparatus (light source: Mercury lamp combined with halogen, 410 W, VT410). A solution of complex (0.01 mmol) in 1,4-dioxane/water (15/5 cm^3) with substrate (10 mmol) and after filling with mixture of N_2 and H_2 [p(H_2) + p(N_2) = 0.1 MPa], was irradiated at 323 K for 6 h. At these conditions liquid phase appeared quite homogeneous. The progress of the reaction was analysed using gas chromatograph (HP model 6890), equipped with a TCD detector and an HayeSep Q column whereas liquid samples were additionally analysed using a gas chromatograph (HP model 6890), equipped with a flame ionization detector (FID) and capillary column, with butan-1-ol or decane as internal standard. Blank tests (reactions in the absence of Rh catalyst precursors or without UV–Vis irradiation) have been performed for all substrates, showing that the respective dehydrogenations do not occur.

2.2. Starting materials

2.2.1. Synthesis of [Rh(η^5-cp)(CO)$_2$]

[Rh(η^5-cp)(CO)$_2$] was prepared according to the modified published procedure [19]. Freshly sublimed [Tl(η^5-cp)] (5.39 g, 20.0 mmol) and [{Rh(CO)$_2$(μ-Cl)}$_2$](0.777 g, 2.00 mmol) were stirred in 150 mL of hexane at room temperature for 24 h. Filtrate from reaction was chromatographed on alumina (5% of H_2O) and orange residue was evaporated under reduced pressure (1.0 Pa) at −40 °C. The product was purified by distillation *in vacuo*, giving dark-orange oil. Yield: 75% (672 mg) based on [{Rh(CO)$_2$(μ-Cl)}$_2$]. IR: ν_{CO} = 2050 and 1988 cm^{-1}. FAB$^+$-MS: *m*/*z* (%) = 168 (50) [Rhcp]$^+$, 196 (30) [M − CO]$^+$, 224 (45) [M]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.45 (s, 5H, cp).

2.2.2. Synthesis of [Rh(η^5-ind)(CO)$_2$]

[Rh(η^5-ind)(CO)$_2$] was prepared by modifying the published procedures [20]. Freshly distilled indene (0.80 mL, 6.98 mmol) was added to solution of buthyllithium (3.50 mL, 1.80 M, 6.3 mmol) in hexane. After cooling to −80 °C the mixture was added to suspension of [{Rh(C_2H_4)$_2$(μ-Cl)}$_2$] (1.20 g, 3.08 mmol) in hexane (25 mL) and stirred at −80 °C for 40 min. Then mixture was allowed to react for 3 h at room temperature. Chromatography of this yellow-brown suspension on alumina-packed column (eluted with hexane) afforded a yellow fraction, which was separated. After removal of the solvent *in vacuo*, the orange residue was dissolved in 15 mL of dichloromethane. An excess of carbon monoxide was bubbled through this solution at room temperature for 2 h. The colour of the solution changed from orange-red to orange. After removal of solvent under reduced pressure, [Rh(η^5-ind)(CO)$_2$] was purified by sublimation at 40 °C *in vacuo*. Yield: 35% (592 mg) based on [{Rh(C_2H_4)$_2$(μ-Cl)}$_2$]. IR: ν_{CO}: 1982 and 2040 cm^{-1}. FAB$^+$-MS: *m*/*z* (%) = 103 (14) [Rh]$^+$, 218 (100) [Rhind]$^+$, 246 (22) [M − CO]$^+$, 274 (27) [M]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (m, 2H, H^{4,7}), 7.19 (m, 2H, H^{5,6}), 6.11(m, 1H, J_{H-Rh} = 3.0 Hz, H^2), 5,81 (m, 2H, H^{1,3}).

2.3. Preparation of the rhodium complexes **1**–**4**

2.3.1. Synthesis of [Rh(η^5-cp)(CO)(PTA)] (**1**)

To an ethanolic solution (15 mL) of [Rh(η^5-cp)(CO)$_2$] (224.0 mg, 1.00 mmol) PTA was added (157 mg, 1.00 mmol) and the mixture refluxed for 2 h. The microcrystalline, yellow product was collected by filtration, washed with cold ethanol (2x5 mL) and hexane (20 mL) and dried *in vacuo*. Yield: **1**, 75% (264.9 mg) based on [Rh(η^5-cp)(CO)$_2$]. Complex **1** is soluble in H_2O ($S_{25\,°C} \approx 4$ mg mL^{-1}), DMSO and chloroform, less soluble in MeOH and EtOH, and insoluble in C_6H_6 and alkanes. **1**, $C_{12}H_{17}N_3OPRh$ (353.17): calcd. C 45.74; H 4.13; N 14.36; found C 45.21, H 4.20, N 15.53. FAB$^+$-MS: *m*/*z* (%) = 168 (50) [Rhcp]$^+$, 325 (47) [M − CO]$^+$, 353 (100) [M]$^+$. IR (**1**, KBr): 2938, 2929, (2s br) ν(CH), 1903 (s) ν(CO), 1704 (m), 1590 (m), 1427 (s), 1280 (m) 1243 (s), 1075 (s), 1015 (s), 1003 (s), 975 (s) 941 (s), 811 (m), 720 (s), 730 (m), 611 (m) and 560 (s) (PTA and cyclopentadienyl bands). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.30 (s, 5H, cp), 4.53 (s, 6H, NCH_2N, PTA), 4.06 (s, 6H, PCH_2N, PTA). ^{31}P{^{1}H} NMR

(121.4 MHz, $CDCl_3$): δ −26.6 (d, $^1J_{P-Rh} = 184.3$ Hz, PTA). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 199.4 (dd, $^1J_{C-Rh} = 85.3$ Hz, $^2J_{C-P} = 23.0$ Hz, CO), 85.3 (d, $^1J_{C-Rh} = 4.8$ Hz, cp), 74.6 (d, $^1J_{C-P} = 15.4$ Hz, PCH_2N), 58.1 (d, $^3J_{C-P} = 5.3$ Hz, NCH_2N).

2.3.2. *Synthesis of [Rh(η^5-cp)(CO){P(CH_2CH_2CN)$_3$}] (**2**)*

To a solution (50 mL) of [Rh(η^5-cp)$(CO)_2$] (224.0 mg, 1.00 mmol) in toluene $P(CH_2CH_2CN)_3$ was added (193.2 mg, 1.00 mmol), and the mixture was refluxed for 6 h. The microcrystalline yellow product was collected by filtration, washed with cold ethanol (2 × 10 mL) and hexane (20 mL) and dried *in vacuo*. Yield: **2**, 52% (202.4 mg) based on [Rh(η^5-cp)$(CO)_2$]. Complex **2** is soluble in DMSO and chloroform, less soluble in MeOH and EtOH, sparingly soluble in H_2O ($S_{25\,^\circ C} \approx 0.5$ mg mL^{-1}) and insoluble in toluene and alkanes. **2**, $C_{15}H_{17}N_3OPRh$ (389.20): calcd. C 46.29, H 4.40, N 10.80; found C 46.11, H 4.31, N 10.90. FAB$^+$-MS: m/z (%) = 103 (100) $[Rh]^+$, 168 (43) $[Rhcp]^+$, 308 (40) $[M - CO{-}CH_2{=}CHCN]^+$, 333 361(70) $[M - CO]^+$, 389(5) $[M]^+$. IR (**2**, KBr): 2966, 2952, 2918 (3s br) ν(CH), 2239 (s) ν(CN), 1906 (s) ν(CO), 1710 (m), 1589 (m), 1425 (s), 1324 (m) 1287 (s), 1075 (s), 1005 (s), 1000 (s), 940 (s) 904 (m), 740 (m), 570 (s) ($P(CH_2CH_2CN)_3$ and cyclopentadienyl bands) ^1H NMR (300 MHz, $CDCl_3$): δ 4.91 (s, 5H, cp), 2.72 (td, $^2J_{H-P} = 14.0$ Hz, $^3J_{H-H} = 7.0$ Hz, 6H, $P(C\underline{H}_2CH_2CN)_3$), 2.16 (td, $^3J_{H-P} = {}^3J_{H-H} = 7.0$ Hz, 6H, $P(CH_2C\underline{H}_2CN)_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 40.5 (d, $^1J_{P-Rh} = 197.2$ Hz, PTA). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ 189.4 (dd, $^1J_{C-Rh} = 80.3$ Hz, $^2J_{C-P} = 24{,}9$ Hz, CO), 119.2 (s, CN) 86.7 (d, $^1J_{C-Rh} = 1.9$ Hz, cp) 25.9 (d, $^1J_{C-P} = 24{,}9$ Hz, PCH_2) 12.5 (s, $\underline{C}H_2CN$).

2.3.3. *Synthesis of [Rh(η^5-ind)(CO)(PTA)] (**3**)*

To an ethanolic solution (20 mL) of [Rh(η^5-ind)$(CO)_2$] (274.1 mg, 1.00 mmol) PTA was added (157 mg, 1.00 mmol) and the mixture was stirred at room temperature for 15 min. The microcrystalline dark-yellow product was collected by filtration, washed with cold ethanol (2 × 5 mL) and diethyl ether (20 mL) and dried *in vacuo*. Yield: **3**, 85% (342.7 mg) based on [Rh(η^5-ind)$(CO)_2$]. Complex **3** is soluble in H_2O ($S_{25\,^\circ C} \approx 6$ mg mL^{-1}), DMSO and chloroform, less soluble in MeOH and EtOH, and insoluble in C_6H_6 and alkanes. **3**, $C_{16}H_{19}N_3OPRh$ (403.22): calcd. C 47.66, H 4.75, N 10.42; found C 47.22, H 4.80, N 10.50. FAB$^+$-MS: m/z (%) = 218 (100) $[Rhind]^+$, 259 (27) $[M - CO{-}ind{-}H]^+$, 260 (18) $[M - CO{-}ind]^+$, 375 (46) $[M - CO]^+$, 403 (76) $[M]^+$. IR (**3**, KBr): 3015, 2970, 2930 (3s br) ν(CH), 1920 (s) ν(CO), 1610 (m), 1450 (m), 1421 (m), 1370 (m), 1290 (m) 1241 (m), 1099 (m), 1015 (s), 975, 971 (s), 924 (s), 894 (m), 811 (m), 770 (s), 731 (m), 695 (m) and 581 (m) (PTA and indenyl bands). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.21 (m, 2H, $H^{4,7}$, ind), 6.95 (m, 2H, $H^{5,6}$, ind), 5.97 (m, 1H, $J_{H-Rh} = 3.0$ Hz, H^2, ind), 5.55 (m, 2H, $H^{1,3}$, ind) 4.47 (s, 6H, NCH_2N, PTA), 4.00 (s, 6H, PCH_2N, PTA). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ −34.0 (d, $^1J_{P-Rh} = 190.0$ Hz, PTA). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 201.0 (dd, $^1J_{C-Rh} = 84.9$ Hz, $^2J_{C-P} = 24.1$ Hz, CO), 124.5 (s, $C^{5,6}$, ind), 120.0 (s, $C^{4,7}$, ind), 114.5 (s, $C^{3a,7a}$, ind), 96.1 (d, $J_{C-Rh} = 4.9$ Hz, C^2, ind), 75.1 (d, $J_{C-Rh} = 2.9$ Hz, $C^{1,3}$, ind), 75.8 (d, $^1J_{C-P} = 15.0$ Hz, PCH_2N), 58.2 (d, $^3J_{C-P} = 3.1$ Hz, NCH_2N).

2.3.4. *Synthesis of [Rh(η^5-ind)(CO){P(CH_2CH_2CN)$_3$}] (**4**)*

To a THF solution (50 mL) of [Rh(η^5-ind)$(CO)_2$] (274.1 mg, 1.00 mmol) $P(CH_2CH_2CN)_3$ was added (193.2 mg, 1.00 mmol) and the mixture was stirred at room temperature for 1 h. The microcrystalline, yellow product was collected by filtration, washed with cold THF (2x10 mL) and pentane (20 mL) and dried *in vacuo*. Yield: **4**, 74% (333.9 mg) based on [Rh(η^5-ind)$(CO)_2$]. Complex **4** is soluble in DMSO and chloroform, less soluble in EtOH and THF, sparingly soluble in H_2O ($S_{25\,^\circ C} \approx 0.7$ mg mL^{-1}) and insoluble in toluene and hexane. **4**, $C_{15}H_{17}N_3OP_3Rh$ (451.15): calcd. C 39.93, H 3.80, N 9.31; found C 40.01, H 3.80, N 9.09. FAB$^+$-MS: m/z (%) = 218 (95) $[Rhind]^+$, 242 (100) $[RhP(CH_2CH_2CN)_2]^+$, 296 (85) $[M - CO{-}ind]^+$, 358 (42) $[M - CO{-}CH_2{=}CHCN]^+$, 411 (97) $[M - CO]^+$, 439 (2) $[M]^+$. IR (**4**, KBr): 2999, 2982, 2945 (3s br) ν(CH), 2240 (s) ν(CN), 1945 (s) ν(CO), 1610 (m), 1459 (m), 1427 (m), 1321 (m) 1232 (s), 1002 (s), 955 (s) 904 (s), 767 (s) 737 (s) ($P(CH_2CH_2CN)_3$ and indenyl bands). ^1H NMR (300 MHz, CD_2Cl_2): δ 7.22 (m, 2H, $H^{4,7}$, ind), 7.21 (m, 2H, $H^{5,6}$, ind), 6.13 (m, 1H, $J_{H-Rh} = 2.7$ Hz, H^2, ind), 5.53 (m, 2H, $H^{1,3}$, ind), 2.36 (td, $^2J_{H-P} = 12.0$ Hz, $^3J_{H-H} = 6.0$ Hz, 6H, $P(C\underline{H}_2CH_2CN)_3$), 2.10 (td, $^3J_{H-P} = {}^3J_{H-H} = 6.0$ Hz, 6H, $P(CH_2C\underline{H}_2CN)_3$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 63.6 (d, $^1J_{P-Rh} = 202.4$ Hz, PTA). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2): δ 193.9 (dd, $^1J_{C-Rh} = 79.1$ Hz, $^2J_{C-P} = 22{,}9$ Hz, CO), 126.3 (s, $C^{5,6}$, ind), 120.0 (s, CN), 117.8 (s, $C^{4,7}$, ind), 115.3 (s, $C^{3a,7a}$, ind), 92.1 (d, $J_{C-Rh} = 5.2$ Hz, C^2, ind), 76.2 (d, $J_{C-Rh} = 3.1$ Hz, $C^{1,3}$, ind), 25.9 (d, $^1J_{C-P} = 24.5$ Hz, PCH_2) 12.1 (s, $\underline{C}H_2CN$).

3. Results and discussion

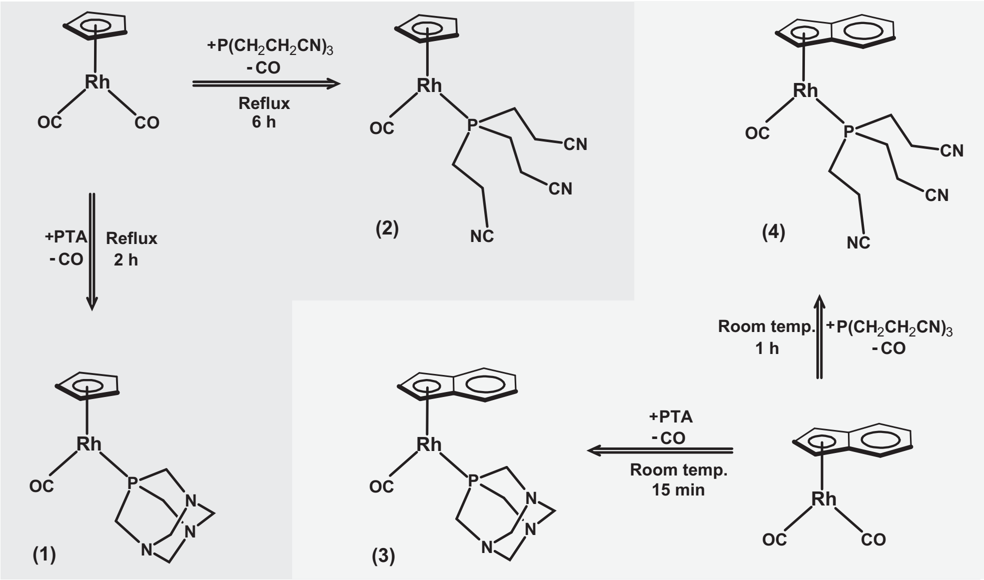
3.1. *Syntheses and characterization*

[Rh(η^5-cp)$(CO)_2$] used for syntheses of phosphine complexes was prepared by modifying the published procedures [19], via the reaction of $[\{Rh(CO)_2(\mu\text{-}Cl)\}_2$ with cyclopentadienyl thallium, whereas [Rh(η^5-ind)$(CO)_2$] was synthesized by the reaction of $[\{Rh(C_2H_4)_2(\mu\text{-}Cl)\}_2]$ with indenyl lithium, followed by carbonylation of the formed [Rh(η^5-ind)$(C_2H_4)_2$], using CO at ambient temperature and pressure [20]. Treatment of [Rh(η^5-cp)$(CO)_2$] with PTA and $P(CH_2CH_2CN)_3$ affords (Scheme 2) [Rh(η^5-cp)(CO)(PTA)] (**1**) and [Rh(η^5-cp)(CO)($P(CH_2CH_2CN)_3$)] (**2**), respectively, while [Rh(η^5-ind)(CO)(PTA)] (**3**) and [Rh(η^5-ind)(CO)($P(CH_2CH_2CN)_3$)] (**4**) are formed in the presence of [Rh(η^5-ind)$(CO)_2$] instead of [Rh(η^5-cp)$(CO)_2$].

Reactivity of [Rh(η^5-ind)$(CO)_2$] for the substitution of phosphine is greater in comparison to [Rh(η^5-cp)$(CO)_2$]. This has been attributed to the flexibility of indenyl ligand to undergo facile η^5–η^3 coordinative isomerizations known as the indenyl effect [21]. All the products were isolated as microcrystalline solids in 52–75% yields, based on [Rh(η^5-R)$(CO)_2$] (R = cp, ind), and characterized by IR and ^1H, ^{31}P, ^{13}C NMR spectroscopies, FAB$^+$-MS and elemental analyses. Compounds **1**–**4** are air stable in the solid state, however their aqueous solutions are stable only under inert atmosphere. Complexes bearing PTA (**1** and **3**) are better soluble in water and other polar solvents, such as MeCN, Me_2SO. Solubility of **2** and **4** in water and alcohols increases in the presence of a trace amount of a base such as sodium hydroxide. All compounds are soluble in medium polarity solvents such as Me_2CO, *n*PrOH, CH_2Cl_2, $CHCl_3$, CH_2Cl_2 and insoluble in non-polar ones such as toluene and hexane.

3.2. *Spectroscopy*

The IR spectra of **1**–**4** show related features with typical vibrations due to the aromatic rings of indenyl or cyclopentadienyl anion, PTA or $P(CH_2CH_2CN)_3$ ligands. The terminal CO ligand in all complexes is easily identified by its characteristic IR stretch (strong and sharp bands in the 1903–1945 cm^{-1} range) which are comparable to those observed in the related complexes [Rh(R)(CO)(PPh_3)] [1957 [22] (R = cp), 1955 [20] (R = ind) cm^{-1}]. On the one hand, the CO stretching frequencies in the cyclopentadienyl complexes are lower than those in the indenyl compounds because of less efficient M–CO back-bonding in indenyl complexes than in cyclopentadienyl compounds [21]. On the other hand, since all these complexes contain the same R ligand (R = cp, ind), the differences found in the CO stretching vibration must derive from the different effects of the phosphine ligands. Indeed, ν(CO) for such a series of complexes increases in the order L = PTA < $P(CH_2CH_2CN)_3$ < PPh_3, revealing a similar trend to that found for the cone angle (θ, deg) [23] of the



Scheme 2. Syntheses of **1**–**4**.

respective phosphines, L = PTA (103) < $P(CH_2CH_2CN)_3$ (134) < PPh_3 (145) [11a,12a]. This is in agreement with the observed [12a] behaviour of the phosphine complexes [Rh(acac)(CO)L] for which ν(CO) increases from the PTA to the PPh_3 complex, PTA thus behaving, as expected, as a weaker π-acceptor than PPh_3. This contrasts with the more sterically demanding phosphine complexes of [Rh(Tpms)(CO)(L)] type [Tpms = $O_3SC(pz)_3^-$ anion], for which ν(CO) decreases from the PTA to the PPh_3 complex [24]. The spectra of all compounds also feature a number of characteristic bands (1100–900 cm^{-1}) associated with the ν(C–X) (X = N, P) vibrations within the phosphine ligands. Besides, several bands due to ν_{as} and ν_s(CH) are also detected in the 3015–2829 cm^{-1} range. In the spectra of **2** and **4**, a strong ν(CN) band of the tris(2-cyanoethyl)phosphine moiety was detected at 2239 and 2240 cm^{-1}, respectively.

The ^{1}H NMR spectra of compounds **1**–**4** show two types of methylene protons in the phosphine region. In the spectra of **1** and **3**, two singlets, assigned to the PCH_2N and NCH_2N protons are observed [11a], while for **2** and **4** two doublets of triplets occur for the PCH_2CH_2CN protons. In the aromatic region, the ^{1}H NMR spectra of **1**–**4** also exhibit appropriate resonances due to the indenyl (**1** and **3**) and cyclopentadienyl (**2** and **4**) anions coordinated to rhodium(I). The $^{31}P\{^1H\}$ NMR spectra are typical for rhodium monophosphine complexes, showing the corresponding doublets in the δ range from −34.0 to 63.6 with the $^{103}Rh–^{31}P$ spin–spin coupling in the 184.3–202.4 Hz range, which are comparable to those observed in the related complex [Rh(ind)(CO)(PPh_3)] {δ 92.5 ppm ($^1J_{P–Rh}$ = 202.6 Hz) [20]}. The ^{31}P NMR spectra of **1**–**4** are suggestive of *P*-coordination of the phosphines to rhodium because of large coordination ^{31}P NMR shift ($\Delta\delta = \delta_{complex} - \delta_{phosphine} = 64 \div 94$ ppm [11a,12a]). In addition, $^{13}C\{^1H\}$ NMR spectra are representative for the coordinated indenyl and cyclopentadienyl anions as well as bound phosphines to metal centre. Moreover, week resonances of terminal carbonyl groups for all complexes were detected in the δ 189.4–201.0 range as doublets of doublets with $^1J_{C–Rh}$ and $^2J_{C–P}$ in the 79.1–85.3 and 22.9–24.9 Hz range, respectively.

The obtained mass spectra confirm the structures postulated for all studied complexes. They exhibit parent ion peaks as well as other peaks, indicating a stepwise loss of the carbonyl group and phosphine for all investigated compounds.

3.3. Catalysis

The complexes **1**–**4** were tested as homogeneous catalyst precursors for the dehydrogenation of propan-2-ol, octane and cyclooctane in one-phase system (Table 1, Fig. 1). Reactions were

Table 1
One-phase dehydrogenation in $H_2–N_2$ atmosphere using UV–Vis irradiation by **1**–**4**.

Substrate	Product	$P_{init}(H_2)^a$ [MPa]	TOF^b [mol substr (h mol Rh)$^{-1}$] (Conversion Yield [%])			
			Complex			
			1	**2**	**3**	**4**
Propan-2-ol	Acetone	0	30.2 (20)	7.5 (4.5)	45 (27)	9 (5.4)
		0.05	15.5 (9.3)	5 (3)	32.5 (19)	4.5 (2.7)
		0.1	7.5 (4.5)	3.5 (2.2)	5 (3)	1.5 (0.9)
Octane	Oct-1-ene	0	25 (15)	6 (3,6)	26 (15.3)	10 (6)
		0.05	6 (3.6)	2 (1.2)	10 (6)	2.5 (1.5)
		0.1	1.5 (0.9)	0.5 (0.3)	2 (1.2)	0 (0)
Cyclooctane	(1Z)-cyclooctene	0	34 (20.4)	25.5 (15.3)	56 (33.6)	22 (13.2)
		0.05	19 (11.4)	17 (10.2)	39 (23.4)	10 (6)
		0.1	2 (1.2)	6 (3.6)	10 (6)	3 (1.8)

Temp. = 323 K; **1**–**4** 0.01 mmol; 1,4-dioxane 15 cm^3; water 5 cm^3; substrate 10 mmol; pH = 10–11 (in presence of NaOH); 6 h.

[a] $p(N_2) = 0.1 - p(H_2)$ [MPa].

[b] TOF – Turnover Frequency; Selectivity 95–98% (for dehydrogenation of propan-2-ol and cyclooctane) and 75–80% (for octane) was calculated by the conversion of substrate to appropriate product.

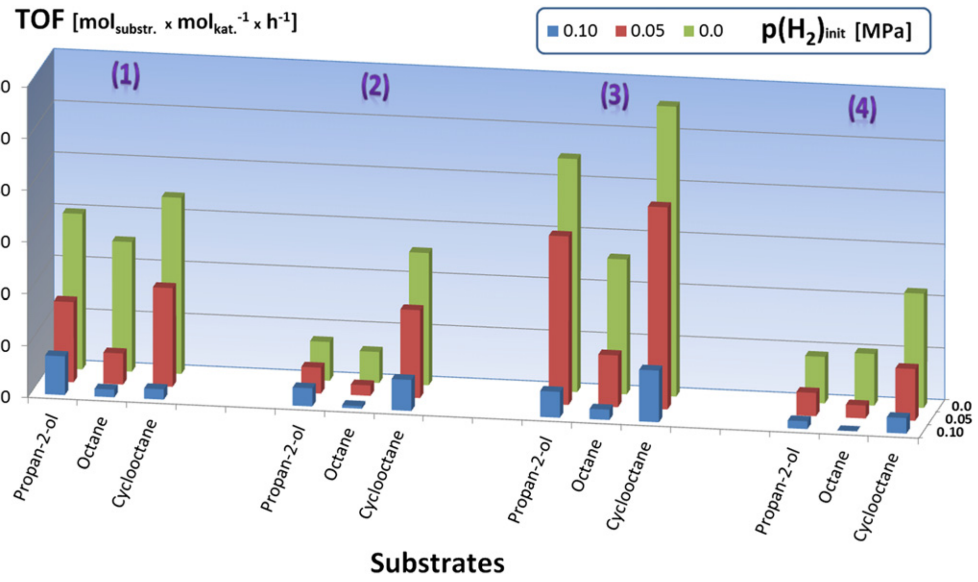


Fig. 1. Correlation between the H_2 pressure and the activity of the corresponding catalyst precursors **1**–**4** in dehydrogenation of propan-2-ol, octane and cyclooctane.

run under photoassisted conditions and without any organic hydrogen transfer acceptor. Substrates for the reactions were chosen based on their prior use in related transformations [8,26,27]. The catalysts showed relatively high activities (maximum TOF of 56 h^{-1}) for homogeneous dehydrogenation reactions in comparison to previously described in literature [7,8,10,26,27]. The rates of dehydrogenation strongly depend on the structure of complexes and decrease in the order **3** > **1** > **4** > **2**. The complexes bearing PTA and indenyl ligands are more active than rhodium compounds with $P(CH_2CH_2CN)_3$ and cyclopentadienyl ligands. Higher reactivity of indenyl complexes in dehydrogenation reactions confirms ability of indenyl ligand to undergo facile η^5–η^3 coordinative isomerizations [21]. Similarly, PTA ligand appears to be more effective ligand for the catalytic process in comparison to $P(CH_2CH_2CN)_3$.

Dehydrogenation reactions under initially dinitrogen atmosphere were more efficient comparing to processes under gaseous mixture of N_2 and H_2, whereas the conversions of substrates were minimal in dihydrogen atmosphere. This suggests reversibility of reaction, depending on conditions. In fact, during dehydrogenation, increasing concentration of the products induces reverse reaction and finally a decrease of the reaction rate was observed. This effect was also detected during dehydrogenation of cyclohexane and cyclooctane with Vaska-type rhodium complex $[RhCl(CO)(PMe_3)_2]$ [10b]. The results of performed catalytic tests confirm the commonly accepted in the literature mechanism of dehydrogenation processes [25]. No catalytic reactions were detected with the absence of base, suggesting involvement of Rh-dihydride complex as a catalytic intermediate [26]. Indeed, ^1H NMR spectra of catalysts after reaction, exhibit resonances as doublets of doublets centred at δ *ca.* −12 ppm, when the base was added. The rate of dehydrogenation of cyclooctane is higher than that for octane, because of the lower value of enthalpy for this process [27]. Dehydrogenation of primary alcohols (methanol, propan-1-ol and hexan-1-ol) to the corresponding aldehydes was unsuccessful in the investigated catalytic system, probably because of the decarbonylation of the products, resulting in an inactive rhodium carbonyl species [28]. On the other hand, during irradiation, loss of CO from the coordination sphere was observed (with and without organic substrate), confirmed by IR spectroscopy. It has been previously proposed, that photolysis of $[RhCl(CO)(PR_3)_2]$ ($PR_3 = PMe_3$ and PPh_3) at the beginning of the catalytic cycle leads to active $[RhCl(PR_3)_2]$, however loss of H_2 might be also photochemically driven [10,29]. Because of high activity of rhodium species formed during irradiation, it was difficult to isolate it from reaction mixture for next run of catalysis. Removing of the organic products by distillation or extraction otherwise separation of catalyst by precipitation resulted in partial decomposition of catalyst.

4. Conclusions

Based on the reaction of $[(\eta^5\text{-R})Rh(CO)_2]$ (R = cp, ind) with water-soluble phosphines, 1,3,5-triaza-7-phosphaadamantane and tris(2-cyanoethyl)phosphine, a suitable way for syntheses of new rhodium(I) complexes of type $[Rh(\eta^5\text{-cp})(CO)(PTA)]$, $[Rh(\eta^5\text{-cp})(CO)(P(CH_2CH_2CN)_3)]$, $[Rh(\eta^5\text{-ind})(CO)(PTA)]$ and $[Rh(\eta^5\text{-ind})(CO)(P(CH_2CH_2CN)_3)]$ was found. All compounds were fully characterized by IR, NMR, FAB-MS spectroscopies and elemental analysis. The solubility and stability in water and organic solvents of the obtained complexes encouraged their further applications in the field of catalysis. In fact, the complexes catalyse the dehydrogenation of saturated compounds under photoassisted conditions without organic hydrogen transfer acceptor, such as another ketone, olefin or halocarbon compounds and, moreover, with the advantage that no high temperature is needed for inducing this process.

An extension of the study towards the synthesis of the $[(\eta^5\text{-R})Rh(CO)(PR_3)]$ (R = cp, ind) compounds with other PTA derivatives, as well as the search for their catalytic activity in aqueous medium, are currently in progress and will be reported elsewhere.

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