NICKEL(0) AND PALLADIUM(0) COMPLEXES WITH 1,3,5-TRIAZA-7-PHOSPHAADAMANTANE. CATALYSIS OF BUTA-1,3-DIENE OLIGOMERIZATION OR TELOMERIZATION IN AN AQUEOUS BIPHASIC SYSTEM

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

New homoleptic nickel(0) and palladium(0) complexes with a water-soluble ligand, 1,3,5-triaza-7-phosphaadamantane, were prepared and characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectra. The complexes, together with the known analogous Ni(0) and Pd(0) complexes with tris(hydroxymethyl)phosphine, were found to be catalysts for buta-1,3-diene oligomerization or telomerization with water in an aqueous biphasic system without a cosolvent or a modifier. Tetrakis[tris(hydroxymethyl)phosphine]nickel (**7**) preferentially catalyzes oligomerization (both linear and cyclic) in the first example of a nickel-catalyzed buta-1,3-diene oligomerization in an aqueous biphasic system. Palladium complexes give telomers or linear oligomers in quantitative yields. In the case of the triazaphosphaadamantane complex **4**, high selectivity to octadienyl ethers (87%) was observed. High values of metal leaching into the product phase in these reactions suggest an easy extraction of starting or intermediate metal complexes caused by the fact that both monomer and products are good ligands for the metal complexes in this particular case.

Key words: Buta-1,3-diene, oligomerization, telomerization; Catalysis in water; Nickel(0); Palladium(0).

Homogeneous catalysis with organometallic complexes in systems containing water has attracted much attention in recent years[1–3] and the field continues to develop at a steady pace. The principal advantage of carrying out the process in a two-phase system with the catalyst in an aqueous phase is the facility with which the products are separated from the catalyst.

Since phosphine ligands are probably the most frequently used ancillary ligands in catalytic systems with transition metals, focus lies on transferring known catalytic processes with phosphine ligands from the organic to the biphasic aqueous medium. Sulfonation of the aromatic rings of triphenylphosphine and other ligands containing phenyl groups, as a straightforward strategy to make the catalytic complex water-soluble, was first used by Chatt[4] many years ago.

While an industrial process based on trisulfonated triphenylphosphine has been known for more than ten years[5] and new sophisticated ligands capable of, *e.g.*, high degree of asymmetric induction have been designed[6], the purification of such ligands for model studies is difficult and tedious[7]. Furthermore, phosphine ligands with sulfonated phenyl rings become even bulkier than the parent phosphines, which may be advantageous in a particular catalytic reaction and disadvantageous in another one. Clearly, a broader spectrum of water soluble ligands is needed and some were indeed prepared and used for catalysis by several groups in the past.

We concentrated our attention on two similar phosphines, *viz.* tris(hydroxymethyl)phosphine (THP) (**1**) first prepared by Chatt *et al.*[8], and 1,3,5-triaza-7-phosphaadamantane (PTA, **2**) first synthesized by Daigle and co-workers[9]. Molybdenum[10,11], tungsten[11], gold[12], rhodium[13–15], and ruthenium[13,16] complexes of 1,3,5-triaza-7-phosphaadamantane were synthesized but nickel and palladium complexes are unknown*. Although Ni(0) and Pd(0) complexes of $P(CH_2OH)_3$ were prepared by Pringle *et al.*[17], they were not used for catalytic purposes.

$P(CH_2OH)_3$

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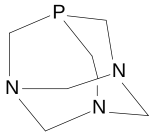

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Complexes of low-valent nickel and palladium are well known as oligomerization and telomerization catalysts for conjugated dienes[18]. The presence of carbon dioxide is reported to be a prerequisite for successful palladium-catalyzed telomerization of buta-1,3-diene with water[19]. In a recent paper, a strong dependence of conversion and selectivity of the reaction in an aqueous biphasic system on the structure of an additional modifier, trialkylamine, was observed[20].

The present work deals with the synthesis of new Ni(0) and Pd(0) complexes of 1,3,5-triaza-7-phosphaadamantane and their use, together with the analogous THP complexes, in the catalysis of butadiene oligomerization or telomerization in an aqueous biphasic system.

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* In the course of the preparation of this paper the authors were informed (A. Kathó, private communication) that such complexes were prepared independently by Darensbourg and co-workers.

EXPERIMENTAL

The syntheses of metal complexes were carried out under an argon atmosphere with standard Schlenk and cannula techniques[21]. Toluene was dried by refluxing with sodium bis(2-methoxyethoxy)aluminum hydride, methanol and ethanol by refluxing with magnesium alkoxide. Tris(hydroxymethyl)-phosphine[17], 1,3,5-triaza-7-phosphaadamantane[9], bis(cycloocta-1,5-diene)nickel[22], tris(dibenzylideneacetone)dipalladium[23], bis[(η^3-2-methylpropen-2-yl)chloropalladium][24], and tetrakis[tris(hydroxymethyl)phosphine]nickel[17] were prepared according to reported procedures as indicated. Buta-1,3-diene (Fluka, 98%) was used as received.

NMR spectra were taken on a Varian UNITY 200 spectrometer at 200.1 MHz, 50.3 MHz, and 81.0 MHz for ^{1}H, ^{13}C and ^{31}P, respectively. Hexamethyldisilane was used as an internal standard for ^{1}H and ^{13}C, external H_3PO_4 was used for ^{31}P. Mass spectra were measured by GC/MS method on a capillary gas chromatograph (Varian, model 3500) equipped with a mass detector (Finnigan MAT, model ITD 800). Nickel and palladium contents in complexes and organic layers after oligomerization/telomerization were determined by atomic absorption spectroscopy on an AAS 3 instrument (Zeiss, Jena, Germany).

Preparation of Complexes

Tetrakis(1,3,5-triaza-7-phosphaadamantane)nickel (**3**). Bis(cycloocta-1,5-diene)nickel (0.43 g, 1.58 mmol) was dissolved in toluene (35 ml) and a solution of 1,3,5-triaza-7-phosphaadamantane (1.0 g, 6.4 mmol) in methanol (3 ml) slowly added with stirring. The off-white precipitate started to form almost immediately. The mixture was further stirred for 1 h and then left to stand overnight. The product was filtered off with a cannula and dried in vacuum. Yield 1.0 g (92%). For $C_{24}H_{48}N_{12}NiP_4$ (687.3) calculated: 8.54% Ni; found: 8.10% Ni.

Tetrakis(1,3,5-triaza-7-phosphaadamantane)palladium (**4**). Tris(dibenzylideneacetone)dipalladium (1.62 g, 1.77 mmol) was dissolved in toluene (250 ml) and a solution of 1,3,5-triaza-7-phosphaadamantane (2.25 g, 14.3 mmol) in methanol (10 ml) was added with stirring which was continued overnight. Yellow-orange compound started to precipitate after 3 h. The precipitate was filtered off with a cannula and dried in vacuum. Yellow-orange powder **5** was obtained (0.6 g, 26%).

The filtrate was concentrated to about half of its original volume and left to stand for 2 days. Another portion of the yellow-orange compound precipitated but since the compound in contact with the mother liquor slowly changed colour to grey, it was left to stand further until all the precipitate turned grey (about 1 week). The precipitate was then filtered off with a cannula and dried in vacuum. Yield 1.9 g (73%) of a grey powder. For $C_{24}H_{48}N_{12}P_4Pd$ (735.0) calculated: 14.48% Pd; found: 14.33% Pd.

Tetrakis[tris(hydroxymethyl)phosphine]palladium (**6**). Solid tris(hydroxymethyl)phosphine (3.25 g, 26.3 mmol) was added with stirring to a hot (about 60 °C) solution of bis[(η^3-2-methylprop-2-enyl)chloropalladium] (1.0 g, 2.54 mmol) in 50 ml of ethanol and dissolved rapidly. The yellow solution was left to cool down to laboratory temperature while stirred for about 1 h during which time it slowly turned red. Orange-red precipitate which formed on cooling was filtered off with a cannula and dried in vacuum. Yield 2.0 g (65%). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the product are in accordance with the published data[17].

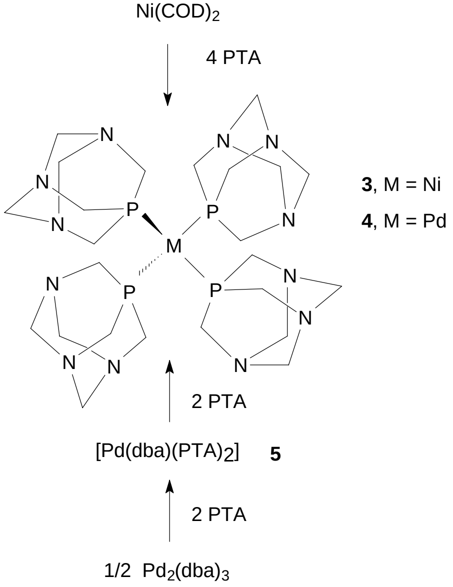
Oligomerization/Telomerization Experiments – General Procedure

A steel rocking autoclave cooled to about –20 °C was charged under argon with butadiene (10.0 g, 0.185 mol) and then with metal complex (0.73 mmol) dissolved in water (25 ml) deaerated by repeated vacuum/argon cycles. The autoclave was placed in a preheated mantle and rocked at 80 ± 3 °C for 20 h. After cooling with water the contents were removed and the layers separated. A sample for metal content determination was taken from the organic layer which was then subjected to analysis by gas chromatography (HP 5890 gas chromatograph equipped with a 50 m × 0.2 mm i.d. quartz capillary column, HP-5 stationary phase) and GC/MS after filtration of a sample through a Cellite layer.

Comparison of retention times and mass spectra of products with those of commercial samples was used for identification of 4-vinylcyclohexene, cycloocta-1,5-diene, (*E,E,Z*)- cyclododeca-1,5,9-triene, and (*E,E,E*)- cyclododeca-1,5,9-triene. The other products were isolated from the higher-scale run (four times) with $[Pd(PTA)_4]$ catalyst after vacuum rectification. The ^1H and ^{13}C NMR spectra of those products are in good agreement with published data[25–29].

RESULTS AND DISCUSSION

New 1,3,5-triaza-7-phosphaadamantane complexes of Ni(0) and Pd(0) were prepared by the reaction of PTA with the appropriate zero-valent complexes with easily displaceable ligands: bis(cycloocta-1,5-diene)nickel ($[Ni(COD)_2]$) and tris(dibenzylideneacetone)dipalladium ($[Pd_2(dba)_3]$), respectively (Scheme 1).



SCHEME 1

While the precipitation of the nickel complex from the methanol–toluene solvent mixture occurs almost immediately, the synthesis of the palladium complex is not so straightforward. Yellow-orange compound **5** precipitates from the same solvent mixture first and is then slowly converted to the desired product. It is insoluble in many common organic solvents both polar and nonpolar, and in water. Fortunately, it is soluble in chloroform, though with slow decomposition (days), and hence NMR spectra could be measured.

A single line in ^{31}P NMR spectrum at δ = –59.8 ppm is the evidence of a phoshorus atom coordinated to palladium with a chemical shift close to that of $[Pd(PTA)_4]$ (see below). Two lines at 4.35 ppm and 4.49 ppm in ^1H NMR spectrum and two lines at 50.46 ppm and 73.19 ppm in ^{13}C NMR spectrum confirm the presence of the PTA ligand. Both proton and carbon-13 NMR spectra show that dibenzylideneacetone ligand is coordinated to palladium; from the proton integrals the ratio PTA : dba = 2 : 1 was calculated. We therefore formulate the yellow-orange compound **5** as $[Pd(dba)(PTA)_2]$.

Phosphorus NMR chemical shifts of $[Ni(PTA)_4]$ and $[Pd(PTA)_4]$ in D_2O were found to be –46.5 ppm and –59.2 ppm, respectively, with the corresponding coordination shifts (relative to the value of –97.9 ppm for free PTA in the same solvent) being 51.4 ppm and 38.7 ppm. Both complexes are air-sensitive even in the solid state, as expected. However, they are stable in water solution for periods of time long enough to measure NMR spectra. In this solution, $[Pd(PTA)_4]$ decomposes to ligand and metallic palladium whereas its nickel analogue decomposes with the formation of 1,3,5-triaza-7-phosphaadamantane *P*-oxide (δ = –2.2 ppm).

^1H NMR spectrum of $[Pd(PTA)_4]$ in D_2O consists of a singlet at 3.79 ppm assigned to protons of the methylene carbons next to phosphorus and an AB system of nonequivalent protons of methylene carbons between nitrogen atoms with chemical shifts calculated at δ 4.41 ppm and 4.49 ppm and $^2J(H\text{-}H)$ = 13.2 Hz. The upfield shift of the former signal relative to the signal of free PTA was not expected since Darensbourg[11] observed a downfield shift of those protons in $M(CO)_5(PTA)$ (M = Mo, Cr, W) complexes. The upfield shift in Ni and Pd complexes is probably due to the high electron density at a low-valent metal centre. Coupling constant $^2J(P\text{-}H)$ approaching zero was observed in accord with the results found with the above complexes. Proton spectrum of $[Ni(PTA)_4]$ gave only very broad lines without any useful information, probably owing to the presence of a paramagnetic impurity.

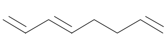
^{13}C NMR spectra of $[Ni(PTA)_4]$ and $[Pd(PTA)_4]$ in D_2O showed signals at 59.52 and 59.24 ppm, assigned to α carbons to phosphorus, and signals at 73.17 and 73.23 ppm assigned to γ carbons. α Carbon signals were broad but no coupling to phosphorus could be resolved.

Tetrakis[tris(hydroxymethyl)phosphine]nickel, **7** was prepared according to the reported procedure[17]; unsatisfactory results were, however, obtained when the synthesis of $[Pd\{P(CH_2OH)_3\}_4]$ was attempted. New route to this complex was developed in which bis[(η^3-2-methylprop-2-enyl)chloropalladium] was reduced by excess $P(CH_2OH)_3$ (Eq. (*1*)).

$$1/2\ [(\eta^3\text{-}C_4H_7)PdCl]_2 + 5\ P(CH_2OH)_3 \longrightarrow [Pd\{P(CH_2OH)_3\}_4] + + CH_2{=}C(CH_3)CH_2P^+(CH_2OH)_3Cl^- \qquad (1)$$

For the butadiene reactions catalyzed by the above Ni(0) and Pd(0) complexes, a simple experimental setup was chosen with the aim of excluding the influence of cosolvents or other agents facilitating phase transfer so that the only variable was the inherent ability of the complex to catalyze the reaction. It is important to note here that THP and PTA themselves are not surfactants in contrast to sulfonated phosphines with ion pair structures; hence, the phase separation is facile.

The ligands are very similar. They are moderately electron donating and their Tolman cone angles[30] were estimated[10,17] to be about 118° (THP) and 102° (PTA); these values lie close to those of trimethylphosphine or triethylphosphine. The main difference between the two phosphines is the ability of the former to create a shell-like network of intramolecular hydrogen bonds in complexes like[17] $[Pd\{P(CH_2OH)_3\}_4]$. We were interested in the possibility that this intramolecular network could govern the catalytic activity or selectivity of the complex.



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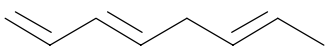

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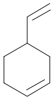

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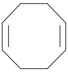

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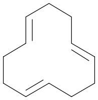

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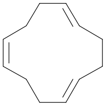

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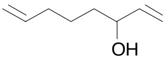

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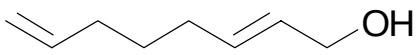

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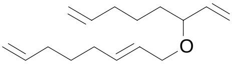

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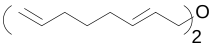

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The results of catalytic experiments are summarized in Table I. Linear (**8**, **9**) as well as cyclic (**10–13**) oligomers and linear telomers (**14–17**) were identified among the products. No reaction was observed with **3** as the catalyst, this complex being the most air-sensitive of **3–7**. Either a small amount of adventitious oxygen during the filling of the autoclave or low thermal stability of the compound is believed to cause the absence of catalytic activity. In all other cases, high yields of products in the absence of carbon dioxide or other modifiers were obtained. The experiments were not optimized and we believe that both reaction time and the amount of catalyst can be decreased without losing much yield.

TABLE I

Oligomerization and telomerization of buta-1,3-diene with water in a biphasic system: buta-1,3-diene/metal ratio = 250, metal concentration 0.03 mol/l, temperature 80 °C, autogenous pressure (autoclave), reaction time 20 h

Catalyst	Yield[a] %	Selectivity to, %												Leaching[b] %
		8	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	Linear trimers	Others[c]	
4	100	4	0	0	0	0	0	2	5	11	76	0	2	63
6	100	49	0	0	0	0	0	2	2	4	31	0	12	42
7	83[d]	24	7	12	5	3	3	0	0	0	0	21	25	15

[a] Oligomers and telomers. [b] The amount of metal in organic phase after the reaction relative to the original amount in the catalyst. [c] According to GC/MS unidentified trimers and tetramers in low yields; polymer was not observed. [d] Gas (probably butadiene) was vented before opening the autoclave.

Nickel complex **7** catalyzes oligomerization, mainly linear, whereas with palladium complexes telomers of butadiene and water form a substantial part of the reaction mixture. To our best knowledge, the first example of nickel-catalyzed oligomerization in aqueous biphasic medium is presented here. The comparison of selectivity of PTA and THP complexes is possible only in the case of palladium complexes. With $[Pd(PTA)_4]$ high selectivity to octadienyl ethers was observed (87%), the other products being also telomers with the exception of 4% of octa-1,3,7-triene. The observed selectivity resembles that found in telomerization of buta-1,3-diene in water emulsion[31] although the ratio between bis(octa-2,7-dienyl) ether and its isomer (octa-2,7-dienyl)(octa-1,7-dienyl) ether is 7 : 1, *i.e.*. much higher than that observed in water emulsion. However, reaction catalyzed by $[Pd(THP)_4]$ gives strikingly different results. The main course of the reaction is linear dimerization and the product distribution is similar to that in single-phase reaction in THF-water mixture catalyzed by $[Pd(PPh_3)_4]$ (ref.[32]). Interestingly, octadienols were only minor products in our experiments.

As mentioned above, the principal advantage of catalysis in aqueous biphasic systems should be the easy separation of catalyst from the products. In our experiments in these model systems without an organic solvent, leaching of metal into organic phase as high as 63% in one run was observed, which prevents the use of the reaction in a continual process. Although leaching of nickel is considerably lower than that of palladium, it is still too high. Our results point to the general problem of the extraction of the catalyst into the organic phase in aqueous biphasic systems in the cases when products are good ligands for the transition metal used.

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