

Conclusions

1. An efficient method has been developed for the preparation of η^4 -diene, η^5 -dienyl, and η^6 -arene complexes of Ir, Os, and Ru, starting with 1,3-cyclohexadiene and the corresponding platinum metal salts.

2. Treatment of 1,3-cyclohexadiene with Na_2OsCl_6 in the presence of SnCl_2 results in the formation of η^4 -cyclohexadiene- η^5 -cyclohexadienyl(trichlorostannyl)osmium, which is a rare example of an organic π -complex containing an Os-Sn bond.

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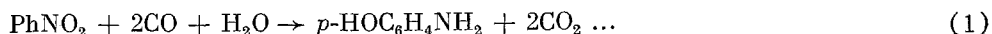
SYNTHESIS AND CATALYTIC PROPERTIES OF PROTONATED CARBONYL-PHOSPHINE

PALLADIUM COMPLEXES

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Solutions of palladium(II) acetate in AcOH in the presence of PPh_3 are able to catalyze the reduction of nitro compounds to the corresponding amines by carbon monoxide under mild conditions. If a two-phase solvent system such as $n\text{-BuOH-H}_2\text{SO}_4$ (5.5 N) is used in place of AcOH, nitrobenzene is reduced to p -aminophenol [1]



The catalyst for this reaction has been proposed to be the complex $[\text{HPd}_2(\text{PPh}_3)_4(\text{CO})(\text{HSO}_4)]_n$, whose composition has been established based on indirect data.

In the present paper we have examined the reduction of $\text{Pd}(\text{OAc})_2$ by carbon monoxide in a system consisting of PPh_3 -organic solvent- HClO_4 , in order to isolate the catalytically active complex in the solid state and study its composition in detail.

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TABLE 1. Spectral and Analytical Characteristics of Complexes Prepared by Reduction of $\text{Pd}(\text{OAc})_2$ in Different Solvents at 40°C in the Presence of PPh_3 and HClO_4 . $\text{Pd}(\text{OAc})_2$ 0.225 g (1 mmole), PPh_3 0.736 (3 mmole), Organic Solvent 10 ml, HClO_4 (4.3 N) 10 ml, CO Flow Rate 0.5-1.0 liter/h, νClO_4^- 1080 cm^{-1}

Solvent	Amount CO_2 evolved, mmole	Yield		Results of elemental analysis			$\nu\text{CO}, \text{cm}^{-1}$	Suggested composition of the complex
		g	%	Pd, %	P, %	P/Pd		
MePh	Traces	—	—	—	—	—	—	Pd(II) complex $\text{HPd}(\text{PPh}_3)_3(\text{ClO}_4)^*$ $\text{HPd}(\text{PPh}_3)_3(\text{ClO}_4) +$ $+ [\text{HPd}_2(\text{PPh}_3)_4(\text{CO}) \times$ $\times (\text{ClO}_4)]_n$
MeCOMe	1.00	0.94	95	10.42	9.1	3.0	None	
EtOH	1.05	0.80	83	11.00	9.3	2.9	1856 v.w	
<i>i</i> -PrOH	1.10	0.70	84	12.71	9.5	2.6	1856 w	Same » » » » $[\text{HPd}_2(\text{PPh}_3)_4(\text{CO})(\text{ClO}_4)]_n$
<i>n</i> -PrOH	0.92	0.73	95	13.87	9.2	2.3	1856 w	
<i>n</i> -BuOH	0.98	0.64	92	15.34	9.0	2.0	1856 s	
<i>n</i> -C ₅ H ₁₁ OH	1.10	0.58	84	15.08	9.1	2.1	1856 s	
<i>n</i> -C ₆ H ₁₃ OH	1.10	0.50	72	15.25	8.9	2.0	1856 s	

*Calc. for $\text{HPd}(\text{PPh}_3)_3(\text{ClO}_4)$: Pd 10.72; P 9.37%.

Experimental

The solvents and HClO_4 used in this study were either analytical grade or chemically pure grade and were used without further purification. PPh_3 was precipitated from conc. HCl prior to use and recrystallized from EtOH.

The isolated complexes were analyzed gravimetrically for Pd [3], spectrophotometrically for P [4], and volumetrically for CO, by measuring the volume of CO evolved upon fusion of a known weight of complex with excess PPh_3 . IR spectra were recorded on a Specord 75IR spectrophotometer using vaseline mulls. Complexes were isolated either in an inert atmosphere or under CO atmosphere. Since the presence of a significant excess of PPh_3 tends to deactivate the catalytic system [2], all of the experiments were carried out at a P/Pd ratio equal to three.

Reduction. $\text{Pd}(\text{OAc})_2$. A reactor was charged with 0.225 g (1 mmole) $\text{Pd}(\text{OAc})_2$, 0.786 g (3 mmole) PPh_3 , and 10 ml *n*-BuOH, and the mixture was stirred for 30 min under a N_2 atmosphere; 10 ml HClO_4 (4.3 N) was then added and CO was bubbled through the reactor at a rate of 0.5-1.0 liter/h as the reactor was thermostatted at 40°C . The course of the reaction was followed by the evolution of CO_2 , which was absorbed by a $\text{Ba}(\text{OH})_2$ solution. Excess $\text{Ba}(\text{OH})_2$ was titrated with acid. The reduction reaction was generally complete after 2 h. After completion of the reaction complex (I), which was lemon yellow colored, was removed by filtration and dried successively with small portions of *n*-BuOH, EtOH, and Et_2O , and then dried under vacuum. Yield 0.64 g (92%). Found, %: Pd 15.34, P 9.0, CO 1.9; P/Pd = 2.03, CO/Pd = 0.43, νCO 1856 cm^{-1} ; νClO_4 1080 cm^{-1} . $\text{Pd}_2\text{P}_4\text{C}_2\text{H}_{10}\text{O}_5\text{Cl}$. Calculated, %: Pd 15.32, P 8.93, CO 2.02. The reduction of $\text{Pd}(\text{OAc})_2$ in other solvents was carried out in an analogous manner and the resulting complexes were isolated and analyzed (Table 1).

Catalytic Reduction of Nitrobenzene by Carbon Monoxide and Water. After completion of the stoichiometric reduction sequence noted above, the reactor was charged with nitrobenzene. The course of the reaction was followed based on the amount of CO_2 evolved.

Preparation of (I) from $[\text{HPd}_2(\text{PPh}_3)_4(\text{CO})(\text{HSO}_4)]_n$ (II). Complex (II) was prepared as a solution in *n*-butanol (10 ml) containing ca. 0.8 mmole Pd [2]. To this solution under an atmosphere of N_2 was added a solution containing 672 mg (2 mmole) $\text{Ba}(\text{ClO}_4)_2$ in 10 ml HClO_4 (2 N). After mixing the resulting lemon-yellow colored precipitate in a layer of butanol and dissolving the BaSO_4 precipitate in water, the butanol layer was separated and washed with water. The precipitate was separated and dried as described above.

TABLE 2. Effect of the Nature of the Solvent on the Reduction of Nitrobenzene by Carbon Monoxide at 40°C. Composition of the Contact Solution: 0.056 g (0.25 mmole) Pd(OAc)₂, 0.1965 g (0.75 mmole) PPh₃, 5 ml HClO₄ (4.3 N), 10 ml Solvent, 1 ml (9.75 mmole) PbNO₂.

Solvent	Amount of CO ₂ evolved (mmole) with time, in min							
	15	30	45	60	75	90	105	120
MePh	—	—	—	—	—	—	—	0,22
MeCOMe	0,21	0,49	0,78	1,13	1,40	1,80	2,01	2,24
EtOH	0,29	0,72	1,10	1,39	1,84	2,37	2,94	3,54
i-PrOH	0,22	0,48	0,80	0,99	1,22	1,41	1,62	1,86
n-PrOH	0,17	0,37	0,60	0,80	1,05	1,30	1,54	2,20
n-BuOH	0,37	0,76	1,17	1,60	2,10	2,60	3,00	3,60
Same *	—	—	—	—	—	—	—	Traces
»†	—	—	—	—	—	—	—	»
n-C ₈ H ₁₇ OH	0,28	0,66	1,00	1,35	1,70	2,04	2,39	2,93
n-C ₈ H ₁₃ OH	0,31	0,73	1,20	1,60	2,03	2,42	2,74	2,97

*Experiment without nitrobenzene.

†Instead of 5 ml 4.3 N HClO₄, 5 ml H₂O was used.

Preparation of (I) from [Pd₂(PPh₃)₄(CO)]_n (III). Complex (III) was synthesized from (II) according to [2]. This complex (200 mg, 0.3 mmole of Pd). 79 mg PPh₃ (0.3 mmole) and 5 ml HClO₄ (4.3 N) were mixed for 1 h under an atmosphere of CO at 40°C. The resulting lemon-yellow colored complex (I) was separated using the method described above. Yield 177 mg or 85% based on Pd. The complex was characterized by IR spectroscopy and elemental analysis.

Preparation of (I) from Pd(PPh₃)₃(CO). Pd(PPh₃)₃CO was prepared according to [5]. This complex (500 mg, 0.54 mmole), 10 ml n-BuOH, and 10 ml HClO₄ (4.3 N) were stirred under CO for 2 h at 40°C. Complex (I) was deposited as a lemon-yellow colored precipitate and was separated as described above. Yield 330 mg (88%).

Preparation of (III) from (I). Freshly prepared complex (I) (0.55 g, 0.8 mmole of Pd) was treated for 1 h under a N₂ atmosphere with a mixture of 15 ml H₂O and 5 ml Py at ca. 20°C. The precipitate was filtered, washed carefully with water, and dried in a vacuum desiccator over H₂SO₄. Yield 0.41 g (80%). Found, %: Pd 16.46, P 9.4; P/Pd = 1.96; νCO 1833 cm⁻¹. Pd₂P₄C₂₃H₆₀O. Calculated, %: Pd 16.51, P 9.62.

Reaction of (I) with PPh₃. Freshly prepared (I) (0.903 g, 1.3 mmole based on Pd) and 3.144 g (12 mmole) PPh₃ were dissolved in 10 ml benzene and stirred for 1 h at ~20°C; the benzene was evaporated under vacuum to dryness, and the residue was treated successively with several portions of 50% alcohol. All of the filtrates were combined and the amount of acid in them was determined by titration. The mole ratio H⁺/Pd obtained in this way was 0.47.

The yellow-green precipitate on the filter was washed with 10 ml C₆H₆ and dried under vacuum. Pd(PPh₃)₄. Found, %: Pd 8.88, P 10.4; P/Pd = 4.02; νCO and νClO₄ absent. PdP₄C₂₂H₆₀O. Calculated, %: Pd 9.21, P 10.74. Yield 1.36 g (91% based on Pd).

Complex (I) was worked up in an analogous manner in EtOH at 40°C. H⁺/Pd ratio found in this way: 0.48; 0.49; 0.57.

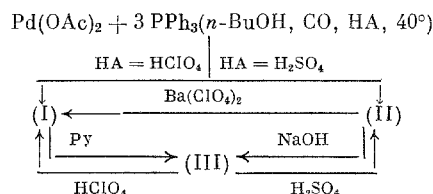
Reaction of (I) with CCl₄. Complex (I) (0.55 g) was treated with 5 ml CCl₄ under Ar. After 1 month the precipitate was removed by filtration and the filtrate was analyzed for CHCl₃ by GLC (LKhM-8MD chromatograph, SE-30 on chromatone, 3 m column, t = 60°C, helium carrier gas flow rate 30 ml/min, catharometer detector).

Results and Discussion

The IR spectra of all the compounds formed in the entire series of solvents (Table 1) contain an intense band in the 1080 cm⁻¹ region, corresponding to vibrations of the ClO₄⁻ anion [6].

$\text{Pd}(\text{OAc})_2$ is not reduced practically at all in toluene, and a $\text{Pd}(\text{II})$ compound is formed. In all of the other solvents studied stoichiometric amounts of CO_2 were obtained and $\text{Pd}(0)$ complexes were isolated. The IR spectrum of the complex obtained upon reduction of $\text{Pd}(\text{OAc})_2$ in *n*-BuOH and higher alcohols contains a band at 1856 cm^{-1} , which may be assigned to $\mu_2\text{-CO}$. This complex has the composition $[\text{HPd}_2(\text{PPh}_3)_4(\text{CO})(\text{ClO}_4)]_n$ (I). Deprotonation of complex (I) could not be achieved in aqueous or alcoholic NaOH solutions. Coordinated CO enters into the reaction with HClO_4 , which leads to decomposition of complex (I). The deprotonated complex (III) $[\text{Pd}_2(\text{PPh}_3)_4(\text{CO})]_n$ could be prepared by treatment of (I) with an aqueous pyridine solution. It should be noted that complex (III) is exceedingly unstable. In organic solvents under a CO atmosphere it is converted to the known cluster $\text{Pd}_4(\text{CO})_5(\text{PPh}_3)_4$, which has a characteristic IR spectrum [5]. Complex (III) can be stored in the solid phase only for a short period of time at low temperatures in an inert gas atmosphere.

CHCl_3 is formed upon treatment of complex (I) with CCl_4 . This reaction is characteristic of transition metal hydrides [7]. The $[\text{HPd}_2(\text{PPh}_3)_4(\text{CO})(\text{HSO}_4)]_n$ complex (II) can be converted to (I) by treatment with $\text{Ba}(\text{ClO}_4)_2$. The overall synthesis and interconversions of all of the isolated complexes can be depicted by the following scheme



Complex (I) reacts with excess PPh_3 to displace CO and HClO_4 from the palladium coordination sphere. $\text{Pd}(\text{PPh}_3)_4$ is formed in high yield (91%) as a result of this reaction, and the displaced acid can be analyzed by titration.

Complex (I) is insoluble in aliphatic hydrocarbons and ether; it dissolves with decomposition in chloroform, 1,2-dichloroethane and acetone. The complex is sparingly soluble in *n*-BuOH, and the solutions are stable in the presence of HClO_4 and a small excess of PPh_3 , which makes it impossible to determine the molecular weight of this compound using the conventional methods. None of the experiments directed to obtaining single crystals of (I) suitable for x-ray structural analysis was successful.

Nevertheless, the results of elemental analysis (H/Pd , $\text{CO/Pd} = 0.5$) and the presence of the bridging carbonyl group (as evidenced by the 1856 cm^{-1} band in the IR spectrum) suggest that this complex is a cluster compound. Calculating the number of valence electrons in the metal skeleton using the accepted rules [8] gives the following results: 30 electrons at $n = 1$, 60 electrons at $n = 2$, 90 at $n = 3$, etc. Most of the binuclear complexes of Pd and Pt which have been described [8] contain 30 valence electrons. The $\text{Pt}[(\text{dppe})_2\text{Pt}_2(\text{H})(\text{CO})][\text{BF}_4]$ complex ($\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) has been reported previously [9], and is analogous to complex (I). The authors have suggested a binuclear structure for it, containing 30 valence electrons. Tetranuclear Pd and Pt clusters contain, as expected, 58 valence electrons, although 60-electron clusters of this type have also been reported [10, 11]. The hexanuclear clusters which have been isolated contain generally 86 electrons. Based on these precedents, the most probable values of n for complex (I) are $n = 1$ or 2. The tetranuclear complex appears to us to be the more favorable one. Stabilization of acid by the exceedingly unstable excess electron complex (III) (60 valence electrons) can be explained in terms of the presence of H^+ in the Pd coordination sphere.

Upon reduction of $\text{Pd}(\text{OAc})_2$ in a mixture of acetone- HClO_4 in the presence of PPh_3 , a light green $\text{Pd}(0)$ complex with a P/Pd ratio of 3 is formed. The IR spectrum of this compound does not contain bands which could be assigned to CO stretching vibrations, but does contain an intense band due to the ClO_4^- stretching vibration [7]. Based on this data, this compound is assigned the composition $\text{HPd}(\text{PPh}_3)_3(\text{ClO}_4)$ (IV). In lower alcohols a mixture of this compound with (I) is obtained.

Catalytic reduction of nitrobenzene by CO can be achieved in all of the solvent systems (Table 2), with the exception of toluene. The fact that the reaction does not take

place in toluene can be attributed to the fact that $\text{Pd}(\text{OAc})_2$ is not reduced in this solvent, and catalytic activity is expressed only by Pd complexes in low oxidation states. In the other solvents studied the catalytic activities do not differ by more than a factor of two. Apparently both the carbonyl complex (I) and the one which does not contain a carbonyl group, (IV), are able to catalyze this reaction. We assume that reduction of nitrobenzene takes place via the participation of coordinated hydrogen.

Conclusions

1. A palladium carbonyl-hydride complex is obtained upon reduction of palladium acetate in the presence of triphenylphosphine and dilute perchloric acid in n-butanol.
2. Reduction of palladium acetate in acetone gives tris(triphenylphosphine)monohydridopalladium perchlorate.
3. Both of these complexes are able to catalyze the reduction of nitrobenzene by carbon monoxide.

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