Journal of Organometallic Chemistry, 202 (1980) C102—C104
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

POLYNUCLEAR CARBONYLTRIALKYLPHOSPHINE COMPLEXES OF ZEROVALENT PALLADIUM

E.G. MEDNIKOV, N.K. EREMENKO,
Department of Biological and Physico-Chemical Problems, Institute of Inorganic Chemistry, 650053 Kemerovo (U.S.S.R.)
and S.P. GUBIN
Institute of Inorganic Chemistry, 630090 Novosibirsk (U.S.S.R.)*

(Received October 8th, 1980)

Summary

The synthesis of three new polynuclear carbonyltrialkylphosphine complexes of Pd^0 is described. The formulae $Pd_{12}(CO)_{15}(PEt_3)_7$, $Pd_{12}(CO)_{15}(PBu_3)_7$ and $Pd_{12}(CO)_{17}(PBu_3)_5$ are proposed for the new complexes.

At present several carbonyltriphenylphosphine complexes of Pd^0 are known, these are $Pd(CO)(PPh_3)_3$, $Pd_3(CO)_3(PPh_3)_4$ and $[Pd(CO)(PPh_3)]_n$ [1]. Attempts to prepare carbonyltrialkylphosphine complexes were unsuccessful, though in some reports the possibility of their formation in solution in the course of the reduction of $Pd(acac)_2$ by triethylaluminium [1] and $Alk_2Pd(PEt_3)_2$ by CO [2] was noted. We have now prepared polynuclear carbonyltrialkylphosphine complexes of Pd^0 as follows [3]:

$$x\mathrm{Pd(OAc)_2} + (x+y)\mathrm{CO} + z\mathrm{PAlk_3} + x\mathrm{H_2O} \xrightarrow[\mathrm{CF_3COOH}]{\mathrm{CH_3COCH_3}}$$

$$\mathrm{Pd}_x(\mathrm{CO})_y(\mathrm{PAlk_3})_z + x\mathrm{CO_2} + 2x\mathrm{HOAc}$$

$x = 12, y = 15, z = 7$, Alk = n-Bu (Bu), Et,
$x = 12, y = 17, z = 5$, Alk = Bu.

To 0.224 g (1 mmol) $Pd(OAc)_2$, 17 ml acetone and 5 ml CF_3COOH were added in a 100 ml vessel, and then 0.5 ml PBu_3 (2 mmol) and 2.5 ml H_2O were added consecutively. The vessel was purged with CO and the reaction mixture was stirred for 3 hours. During the reaction the stoichiometric quantity of CO_2 was given off. The complex was washed with EtOH and dried in vacuo for one hour. Yield 85%.

TABLE 1

ELEMENTAL ANALYSES AND MOLECULAR WEIGHTS FOR CARBONYLTRIALKYLPHOSPHINE CLUSTERS OF Pd^0

Mole ratio	Analyses (%)					M
	Pd	C	H	P	CO	
$Pd:PBu_3$						
1:1.5	46.53	32.22	4.91	5.67	17.14	2800
1:2.5	46.28	33.00	4.79	5.54	17.23	2820
1:3.1	44.56	34.82	5.30	5.70	16.50	—
1:3.3	43.04	35.87	5.70	6.30	15.37	3060
1:4	40.99	38.77	6.10	—	13.77	3200
1:5	40.82	38.28	6.36	—	13.69	3200
1:10	40.71	37.43	5.92	—	14.14	3310
1:15	40.20	38.12	6.23	—	13.44	3870
$Pd:PEt_3$						
1:3.3	50.80	27.06	3.99	—	17.42	2070[a]
1:10	50.62	27.39	4.47	—	17.49	—
1:15	50.52	27.08	4.12	—	17.32	—
Calculated for						
$Pd_{12}(CO)_{17}(PBu_3)_5$	46.19	33.45	4.92	5.60	17.22	2765.07
$Pd_{12}(CO)_{15}(PBu_3)_7$	41.02	38.19	6.12	—	13.49	3113.70
$Pd_{12}(CO)_{15}(PEt_3)_7$	50.59	27.12	4.19	—	16.64	2524.56

[a] For $Pd:PEt_3$ = 1:4, in benzene.

On the basis of elemental analyses volumetric analyses of CO and molecular weights determination (Table 1) it was found that $Pd_{12}(CO)_{17}(PBu_3)_5$ was mainly formed at a mole ratio $Pd:PBu_3$ = 1:1.5-1:3 and $Pd_{12}(CO)_{15}(PBu_3)_7$ at a mole ratio $Pd:PBu_3$ = 1:4—1:10 (for a 100 ml vessel*). Optimum ratios for these complexes are $Pd:PBu_3$ = 1:1.5—1:2.5 and $Pd:PBu_3$ = 1:5—1: 10, respectively. $Pd_{12}(CO)_{15}(PEt_3)_7$ was prepared at a ratio $Pd:PEt_3$ = 1:3.3—1:15. Although a comparison of Pd analysis results for complexes prepared at a ratio $Pd:PBu_3$ = 1:4-1:10 by *F*-criterion ($P = 0.95$) shows insignificant variation, the decrease of metal content on changing the ratio $Pd:PBu_3$ = 1:4 to 1:15 is noteworthy. This decrease was observed to an even greater extent on transition from a ratio $Pd:PBu_3$ = 1:1.5 to 1:3, so the preparation of complexes of other compositions at these ratios is not excluded. Therefore the formulae given in this report are the best approximation to the experimental facts and require X-ray definition.

The complexes appear to be of cluster nature. They are dark red crystalline powders stable under CO. The carbonyltributylphosphine complexes of Pd^0 are readily soluble in saturated hydrocarbons, unlike the carbonyltriethylphosphine complexes. The low molecular weight results for $Pd_{12}(CO)_{15}(PEt_3)_7$ are due to the lower stability of its benzene solution compared with the solution of $Pd_{12}(CO)_{15}(PBu_3)_7$ in cyclohexane, which could be detected in the IR spectra of these solutions.

IR and ^{31}P NMR spectra also confirm the formation of these compounds in the ratios given above. IR spectra of $Pd_{12}(CO)_{17}(PBu_3)_5$ and $Pd_{12}(CO)_{15}(PBu_3)_7$ are characterised by a strong band at 2034 cm^{-1} for the first compound and by a weak band of the same frequency for the second, attributed to terminal CO groups. The vibrations of the bridging CO groups of the first compound,

---

*The composition of the products also depends on the partial pressure of CO.

at 1914, 1898, 1871 and 1818 cm^{-1}, are shifted relative to the bands of the bridging CO groups of the second compound, 1890, 1852, 1800 cm^{-1}. This is in accordance with the accepted model of the M—π-acceptor ligand bond [4], if we take into account the decrease in number of phosphine ligands. The ν(CO) frequencies of $Pd_{12}(CO)_{15}(PEt_3)_7$ are in the same region as those of $Pd_{12}(CO)_{15}(PBu_3)_7$ except for a shift of the terminal CO band to 2051 cm^{-1}. The ^{31}P NMR spectrum of $Pd_{12}(CO)_{17}(PBu_3)_5$ exhibited one signal at τ −5.0, while ^{31}P NMR spectra of $Pd_{12}(CO)_{15}(PBu_3)_7$ and $Pd_{12}(CO)_{15}(PEt_3)_7$ had two signals at $\tau_1 = -4.0$ and $\tau_2 = +3.3$ (~2:1) for the first compound, and at $\tau_1 = -11.0$ and $\tau_2 = -3.1$ (~2:1) for the second. $\Delta\tau = \tau_2 - \tau_1$ is approximately the same for the PBu_3 (7.3) and PEt_3 (7.9) compounds.

Addition of two equivalents PBu_3 to a solution of $Pd_{12}(CO)_{17}(PBu_3)_5$ in cyclohexane under CO resulted in the evolution of two moles of CO. The IR spectrum obtained after this addition was identical to that of a solution of $Pd_{12}(CO)_{15}(PBu_3)_7$ in cyclohexane.

A characteristic property of these complexes is their susceptibility to complete substitution of the ligands to yield PdL_4 and PdL_3. This method was used to prepare the complexes $Pd(PPh_3)_4$, $Pd(AsPh_3)_4$, $Pd(SbPh_3)_4$, $Pd[P(OPh)_3]_4$ etc.

IR spectra were recorded in Nujol or in cyclohexane or benzene on a 'Specord - 75IR' spectrophotometer. ^{31}P-{H} NMR spectra were recorded in cyclohexane and benzene at room temperature using a 'Bruker SXP 4-100' spectrometer. Chemical shifts were measured with respect to 85% H_3PO_4. CO analyses were made by melting complexes with excess of PPh_3 in an inert atmosphere. Molecular weights were determined cryoscopically in Ar-blanketed cyclohexane.

We thank Drl V.I. Sokolov for helpful discussion.

References

1 A. Misono, Y. Uchida, M. Hidai and K. Kudo, J. Organometal. Chem., 20 (1969) 7.
2 T. Ito, H. Tsuchiya and A. Yamamoto, Bull. Chem. Soc. Jap., 50 (1977) 1319.
3 E.G. Mednikov and N.K. Ermenko, Koord. Khim., in press.
4 L. Malatesta and S. Cenini, Zerovalent Compounds of Metals, Academic Press, London, 1974.