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Carbonyl Complexes of Palladium Stabilized on Phosphinated Polymer Supports

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The reactions of carbon monoxide with salts of palladium(II) are complex, frequently giving ill-defined complexes or mixtures of complexes in formal oxidation states 0 to +2 [1, 2]. Neutral, mononuclear carbonyl complexes of palladium are both rare and, when known, are normally labile. No well-defined, neutral carbonyl complex of palladium(II) has been described [2]. The use of polymer chains with Lewis base anchor-sites to immobilize metal complexes in discreet and sometimes otherwise unattainable environments is well established [3]. As part of a continuing study of the structures and catalytic activities of such systems [4], we herein report results of an investigation into the interaction of palladium (II) with carbon monoxide and triphenylphosphine or polymers with Ph_2P-anchor-sites.

A solution of $PdCl_2(PhCN)_2$ in benzene was stirred at room temperature under an atmosphere of CO for three days. On reducing the volume of the solution under a stream of CO and subsequent dilution with methylcyclohexane, $[PdCl_2(CO)(PhCN)]$, (*1*), was thrown down as an impure brown powder. The material showed infra-red bands at 2295 (m, PhCN), 1990 (vw), 1947 (vs, CO) and 327 (Pd–Cl) cm^{-1}, which are consistent with the postulated formula. The material decomposed over 100 °C to yield CO (8.3%, Calc. 9.08%). The CO evolved was sequentially purified by gas chromatography, methanated, and detected and estimated using a flame-ionisation detector. This method has been found to be both rapid and simple for the estimation of CO [5] and was used throughout this study.

Reaction of $[PdCl_2(PhCN)_2]$ with CO and subsequent treatment with an equimolar amount of triphenylphosphine gave (Eq. 1) the known dinuclear complex $[Pd_2Cl_4(PPh_3)_2]$, (*2*) [6].

$$2PdCl_2(PhCN)_2 + 2PPh_3 \xrightarrow{CO} Pd_2Cl_4(PPh_3)_2 + 4PhCN \quad (1)$$

No monosubstituted carbonyl or benzonitrile complex was observed. Attempts to prepare a mononuclear complex by the reaction of the dinuclear, chlorine-bridged complex *2* with CO, or by the reaction of a solution of *1* with an equivalent amount of PPh_3, failed. These observations showed that, for mobile complexes, reaction 2 (Y = CO or PhCN) proceeds readily to the left. This result is in contrast to the facile preparation of the analogous complexes of platinum(II), *cis*-$[PtCl_2(CO)(PR_3)]$ (R = Et, Pr, Bu), from $[Pt_2Cl_4(PR_3)_2]$ and CO [7]:

$$Pd_2Cl_4(PPh_3)_2 + 2Y \rightleftharpoons 2PdCl_2(Y)PPh_3 \quad (2)$$

In an inert atmosphere and at room temperature, reaction of $[PdCl_2(PhCN)_2]$ with a polymer-chain with Ph_2P-anchor-sites gave the monosubstituted product (Eq. 3) (*cf.* ref. 8, 9). The retained benzonitrile ligand was labile and was readily displaced by carbon monoxide (Eq. 4) or solvent. These data indicated that immobilization of palladium complex moieties at tertiary phosphine anchor-sites discouraged the formation of the chlorine-bridged dinuclear complexes characteristic of monophosphines.

$$PdCl_2(PhCN)_2 + PPh_2(polymer) \rightarrow PdCl_2(PhCN)(PPh_2polymer) \quad (3)$$

$$PdCl_2(PhCN)(PPh_2polymer) + CO \rightarrow PdCl_2(CO)(PPh_2polymer) \quad (4)$$

Phosphinated polymers with styrene, epichlorohydrin, or vinyl alcohol backbones, prepared by published procedures [4], have been used. In cases when the phosphinated polymer contained some residual chlorine allowance had to be made for such chlorine when estimating the stoicheiometry of the attached complex. Consequently, estimations for chlorine–palladium ratios are more tenuous than other estimations. The analytical results (Table I) demonstrate that attachment of palladium occurred at a large fraction of the available anchor-sites.

That the complexes prepared at room temperature from polystyrene or epichlorohydrin were dichloropalladium(II) complexes with benzonitrile or carbon monoxide ligands was demonstrated by chlorine–palladium ratios and by the observation in the infrared spectra of bands in the respective regions 2250–2300 or 1930–1965 cm^{-1}. Bands were observed in the region 320–350 cm^{-1}, which have been tentatively assigned as terminal palladium–chlorine bands, but which are close to polymer bands in the same region [10].

Thermal decomposition of the carbonyl complexes, and analysis of the gaseous products, demonstrated the ratios CO/Pd = 0.3–1.0. The carbonyl complexes were thermally stable up to approximately

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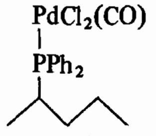
TABLE I. Analytical and Spectroscopic Data.

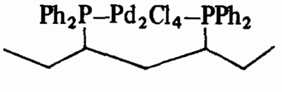
Polymer[a]	Atm.	Time	Elemental Analyses (%)			Ratios				Color	Infra-red Spectra (cm^{-1})[b]		
			Cl	P	Pd	CO[c]	P/Pd	Cl/Pd[d]	CO/Pd		PhCN	CO	Pd–Cl[e]
At 20 °C													
Styrene	CO	3d	14.53	5.16	10.61	2.2	1.7	1.9	0.8	Purple-brown	–	1964	339
Styrene (2% crosslinked)	CO	1d	6.25	2.78	9.57	0.8	1.0	2.0	0.3	Reddish-brown	–	1947	324
Styrene (2% crosslinked)	N_2	1d	4.80	3.17	7.28	0	1.5	2.0	0	Light tan	2291	–	325
Vinyl Alcohol[f]	CO	1d	6.22	10.18	10.71	2.7	3.3	1.5	1.0	Reddish-brown	–	1949	334
Vinyl Alcohol[g]	CO	15 min	6.12	7.77	9.31	n.m.	2.9	2.0	n.m.	Brown	2296(w)	1944	329
Vinyl Alcohol[g]	CO	1d	7.18	5.69	19.02	4.1	1.0	1.1	0.8	Brown	–	1949	337
Vinyl Alcohol[f]	N_2	2d	7.01	10.72	9.56	0	3.85	2.0	0	Light tan	–	–	333
Epichlorohydrin	CO	3d	21.68	4.64	15.80	1.7	1.0	1.7	0.4	Purple-brown	–	1951, 1930(sh)	342
Epichlorohydrin	N_2	2d	23.19	5.15	12.00	0	1.5	2.2	0	Light tan	2287(w)	–	345

[a] Monomer unit of polymer backbone; not all units were substituted with Ph_2P-anchor-sites. [b] Nujol mulls; (w) = relatively weak peak. [c] Thermal decomposition. [d] After allowing for unsubstituted chlorine bonded to the polymer in appropriate cases. [e] Tentative assignments; there are polymer bands in the same region. [f] With -OPPhO-anchor sites. [g] With Ph_2PO-anchor sites.

100 °C. The lower ratios (CO/Pd) cannot therefore be attributed to thermal instability. A possible explanation of these observations is that complexes bonded at relatively isolated anchor-sites are mononuclear (A), but that, at suitably proximate pairs of anchor-sites, dinuclear complexes are formed (B). A recent report [11] has described $PdCl_2$ immobilised on a polymer with amine anchor-sites. The Pd species in this system was thought to be three-coordinate [11]. The above results suggest that the molar ratio of CO which may be complexed by palladium can be used to demonstrate the fraction of mononuclear palladium complex moieties.



(A)



(B)

Only when the polymer support was derived from poly(vinyl alcohol) did a significant proportion of the product formed over long periods of time appear to be a carbonyl complex of palladium in an oxidation state lower than +2. The only difference to which this consequence may be attributed is that, in these cases, the polymer anchor-sites were of phosphinite character, instead of a tertiary phosphine.

In a related study we have observed the facile reduction at room temperature of similar complexes of platinum(II), and formation of complexes of platinum(0) (Ph_2P–/Pt $\lesssim$ 1.0) related to known cluster systems [12].

The catalytic utility of the above complexes will be described in a subsequent paper.

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