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Thermolysis of Tetranuclear Palladium Clusters: Unexpected Transfer of Oxygen from a Carboxylate Group to Carbene and Carbonyl Bridging Ligands; Carbon Dioxide Insertion into C–H Bonds

Tatiana A. Stromnova, Irina N. Busygina, Natalya Yu. Tihonova and Ilya I. Moiseev*

N. S. Kurnakov Institute of General and Inorganic Chemistry, USSR Academy of Sciences, Moscow 117907, USSR

Thermolysis of the tetranuclear palladium clusters $[Pd_4(\mu\text{-}Q)_4(\mu\text{-}O_2CR)_4]$ ($Q = CPh_2$ or CO; R = Me, CMe_3, Ph, CH_2Cl or CF_3) has been found to involve inner-sphere oxidation of carbene or carbonyl ligands during which an oxygen atom transfer occurs from the carboxylate group to the carbene or carbonyl ligand; the thermolysis of the carbonyl clusters gives rise to the products of CO_2 insertion into the C–H bond of benzene or toluene used as solvents forming benzoic acid from benzene and a mixture of phenylacetic and toluic acids from toluene.

Thermolysis of carbonyl clusters of Os, Ru, Mo, W and Ni is known to result in CO elimination and formation of higher nuclearity clusters.[1,2] In this paper the thermolysis of the tetranuclear carbonyl or carbene palladium clusters $[Pd_4(\mu\text{-}Q)_4(\mu\text{-}O_2CR)_4]$ with a square metal skeleton ($Q = CPh_2$ or CO; R = Me, CMe_3, Ph, CH_2Cl or CF_3)[3–5] is discussed.

$$[Pd_4(\mu\text{-}CPh_2)_4(\mu\text{-}O_2CR)_4]$$

1 R = Me
2 R = Ph
3 R = CH_2Cl
4 R = CF_3

Thermolysis of the palladium–carbene complexes $[Pd_4(\mu\text{-}CPh_2)_4(\mu\text{-}O_2CR)_4]$ **1–4** was carried out in benzene solution under an argon atmosphere.† The main products of this reaction in the case of complex **1** were found to be benzophenone (70–90%) and small amounts of biacetyl and CO [eqn. (1)].

$$\underset{\mathbf{1}}{[Pd_4(CPh_2)_4(O_2CMe)_4]}\rightarrow Pd + Ph_2C{=}O + MeCOCOMe + CO + \cdots \quad (1)$$

The acetate group is the only source of oxygen in the reaction under consideration so benzophenone would be expected to be formed from oxygen atom transfer from the acetate group to diphenylcarbene [eqn. (2)].‡ The acetyl groups formed either

$$\{Ph_2C{:}\} + \{MeCO_2\}\rightarrow Ph_2C{=}O + \{MeCO\} \quad (2)$$

dimerize giving biacetyl or undergo decarbonylation [eqn. (3)].

$$\begin{array}{l}\{MeCO\}\rightarrow MeCOCOMe\\ \downarrow\\ CO + \cdots\end{array} \quad (3)$$

The transfer of an oxygen atom from the acetate group to the diphenylcarbene ligand seems to be a rather unusual process. The acetate group and acetic acid itself are considered to be thermodynamically very stable compounds, and so it would not be expected that acetate groups would behave as oxidants or oxygen sources with the carbene ligands.

Thermolysis of the related carbene complexes **2–4** in benzene solution in the absence of dioxygen yields benzophenone *via* diphenylcarbene oxidation with the oxygen atoms of carboxylate groups [eqn. (4)].

$$[Pd_4(CPh_2)_4(O_2CR)_4]\rightarrow Pd + Ph_2C{=}O + \{RCO\} \quad (4)$$

The transfer of oxygen from the carboxylate group to the bridging neutral ligand was found to be common for Pd^+ carbonyl clusters as well. For instance, thermolysis§ at 110 °C of the comparatively stable carbonylpalladium carboxylates $[Pd_4(CO)_4(OCR)_4]$ **5–9** yields CO_2 which is a product of oxidation of the neutral CO ligand with oxygen of the carboxylate group [eqn. (5)].

$$[Pd_4(CO)_4(O_2CR)_4]\rightarrow Pd + CO_2 + \{RCO\} \quad (5)$$

5 R = Me
6 R = CF_3
7 R = CH_2Cl
8 R = Ph
9 R = Bu^t

Thermolysis of complex **5** gave some biacetyl, the product of

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† The complex (1 mmol) and benzene (2 ml) were placed in a 10 ml glass tube, which was evacuated, filled with argon, sealed and placed in thermostat at 80 °C for 1–2 h. Products were identified and quantitated by GC–MS and GLC.

‡ The braces { } denote the groups undergoing reactions, without the metal fragment.

§ The complex (2 mmol) and benzene (10 ml) were placed in an 80 ml glass tube, which was evacuated, filled with argon, sealed and thermostatted at 110 °C for 5–6 h. Products were identified and quantitated by mass spectrometry, GC–MS and GLC.

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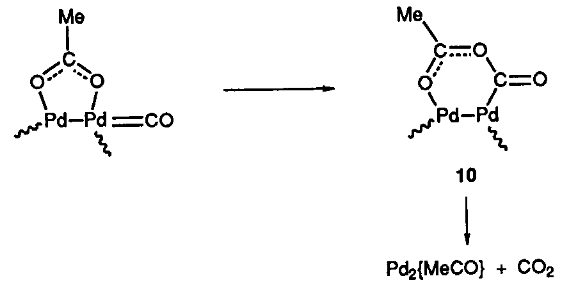

Scheme 1

acetate group reduction. Therefore, the reaction under consideration could be formally depicted as consisting of oxidative [eqn. (6)] and reductive [eqns. (7) and (8)] processes.

$$4AcO^- \longrightarrow 2Ac_2 + 4O + 4e^- \quad (6)$$
$$4CO + 4O \longrightarrow 4CO_2 \quad (7)$$
$$4Pd^+ + 4e^- \longrightarrow 4Pd \quad (8)$$

All the reactions involving oxygen atom transfer from carboxylate groups to diphenylcarbenes in complexes **1–4** and those to CO in complexes **5–9** are assumed to be of the same type. It is possible that both sets of reactions proceed *via* a similar mechanism. For example, CO oxidation with the oxygen of carboxylate group might involve CO insertion into metal—oxygen bonds (Scheme 1).

The decomposition of the unstable intermediate **10** could take place with formation of a reduced form of palladium and coordinated acetyl groups.

Reactions similar to those in Scheme 1 involving the insertion of diphenylcarbene into palladium—oxygen bonds following inner-sphere carbene oxidation are likely to give the products obtained in the thermolyses of the diphenylcarbene complexes.

Equation (5) does not depict the carbonylpalladium carboxylate thermolysis completely. The yield of CO_2 is 10–15%. The majority of the CO_2 which is expected to be formed from CO oxidation was found as benzoic acid¶ (yield 60–70%) when the thermolysis of complexes **5–9** was carried out in benzene solution [eqn. (9)].

$$\underset{\textbf{5–9}}{[Pd_4(CO)_4(O_2CR)_4]} + PhH \rightarrow Pd + CO_2 + PhCO_2H + \cdots \quad (9)$$

Even more unexpected results were obtained when the thermolysis of complex **5** was studied in toluene. In this case, apart from the isomeric toluic acids which are the products of CO_2 insertion into aryl–hydrogen bonds, phenylacetic acid, the product of CO_2 insertion into toluene alkyl C—H bonds was formed [eqn. (10)].

$$\begin{array}{l}[Pd_4(CO)_4(OAc)_4] + PhMe \rightarrow Pd + CO_2 + PhCH_2CO_2H \quad (10)\\ \quad\downarrow \\ Pd + CO_2 + MeC_6H_4CO_2H\end{array}$$

Benzoic acid formation from benzene and CO_2 is not favourable thermodynamically (ΔG°_{298} + 5.96 kcal mol^{-1}; 1 cal = 4.184 J). Under our experimental conditions the energy losses associated with benzoic acid formation are compensated by the energy gained in palladium reduction.

The results discussed show that reactivity of carbonyl clusters is similar to that of carbene clusters, though no products of benzophenone insertion into C—H bonds were found in reaction mixtures after thermolysis of diphenylcarbene clusters.

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¶ After the thermolysis in benzene solution, the solution was filtered to remove metallic palladium and solvent was removed *in vacuo*. The non-volatile white residue (benzoic acid) was identified by its m.p. and mass spectrometry. The products of thermolysis in toluene solution were analysed using the same procedure. The composition of the non-volatile residue (mixture of toluic and phenylacetic acids) was determined by mass spectroscopy (Kratos MS890). The organic compounds were identified by mass spectrometric comparison.[6]