The Mechanism of Formation of the Cluster $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^{2+}$

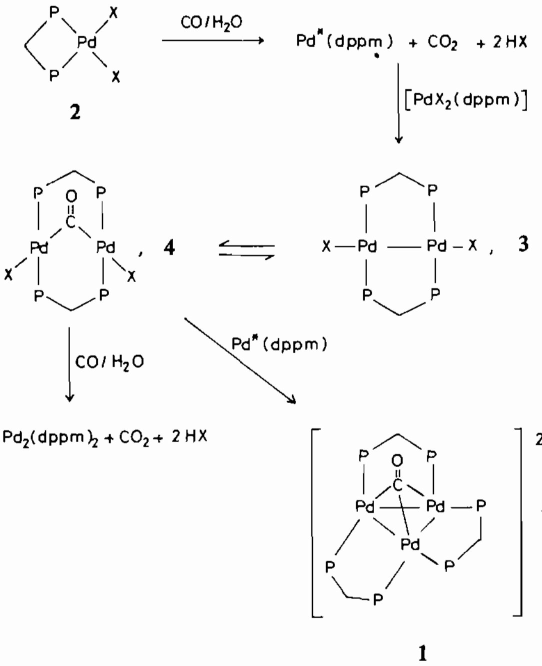
BRIAN R. LLOYD and RICHARD J. PUDDEPHATT

Department of Chemistry, University of Western Ontario, London, Ont. N6A 5B7, Canada

Received July 23, 1984

The rational synthesis of metal cluster complexes from monomeric precursors requires a knowledge of the mechanisms of cluster formation, but relatively few cluster systems have proved to be suitable for such mechanistic studies [1]. As a contribution to palladium cluster chemistry [2], we have studied the mechanism of formation of $[Pd_3(\mu_3\text{-}CO)(\mu\text{-}dppm)_3]^{2+}$, **1**, dppm = $Ph_2PCH_2PPh_2$, whose synthesis and structure have been described earlier [3].

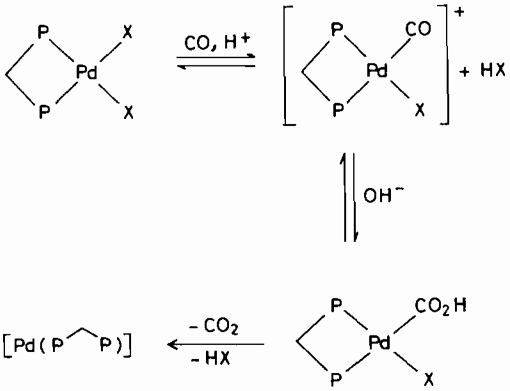
Complex **1**, as the trifluoroacetate salt, was initially prepared by reaction of CO with a solution of $Pd(OAc)_2$, dppm, and excess CF_3CO_2H in aqueous acetone [3]. It has now been shown that the initial solution contains $[Pd(O_2CCF_3)_2(dppm)]$, **2**, and that the reduction of **2** by CO/H_2O involves intermediate formation of $[Pd_2(O_2CCF_3)_2(\mu\text{-}dppm)_2]$, **3** and $[Pd_2(O_2CCF_3)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, **4**. Complexes **2** and **3** have been isolated in pure form and fully characterized*, and the reversible addtition of CO to **3** to give **4*** has been monitored separately by IR, ^1H and ^{31}P NMR spectroscopies [4]. The overall reaction of **2** to give **1** can be monitored using $^{31}P\{^1H\}$ NMR spectroscopy as shown in Fig. 1. From the overall stoichiometry, reduction of one mol of **2** to **1** should give 0.67 mol of CO_2 and was observed to give 0.78 ± 0.02 mol of CO_2. It is possible that some catalysis of the Water Gas Shift reaction may account for the slight discrepancy in CO_2 yield. Reduction of pure **3** to **1** by CO/H_2O under the same experimental conditions does occur, but this was slower than reduction of **2**. Increasing the concentration of water increases the rate of reduction of **2**, but increasing the concentration of CF_3CO_2H leads to some decrease in rate. From these experiments, the mechanism of Scheme 1 is proposed.



Scheme 1. Proposed mechanism for formation of the cluster complex **1** ($X = CF_3CO_2$).

The reduction of **2** involves the overall reaction of eqn. 1 [5] and, in a mechanistic sense, probably proceeds according to eqn. 2, $X = CF_3CO_2$.

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e^- \qquad (1)$$



(2)

The reaction is aided by the good leaving group, $CF_3CO_2^-$, which allows co-ordination of CO. This reduction is presumably faster with the palladium(II) precursor, **2**, than with the dipalladium(I) precursor, **3** or **4**. Since this reduction, giving a very reactive palladium(0) intermediate, is almost cer-

---

*Spectroscopic data: for **2**; ^1H NMR; $\delta(CH_2P)$ 4.69, t, $^2J(PH)$ 11; ^{31}P NMR; $\delta(P)$ −48.2, s. For **3**; ^1H NMR: $\delta(CH_2P)$ 4.35, quintet, ^2J + $^4J(PH)$ 4; ^{31}P NMR; $\delta(P)$ −9.4, s. For **4**, ^1H NMR; $\delta(CH^AH^BP)$ 3.68 *and* 3.11 $^2J(H^AH^B)$ 14.5; ^{31}P NMR; $\delta(P)$ 18.3, s; IR; $\nu(CO)$ 1710 cm^{-1}. For **5**, ^1H NMR; $\delta(CH_2P)$ 5.34, quintet, ^2J + $^4J(PH)$ 5; ^{31}P NMR; $\delta(P)$ −36.8, s.

0020-1693/84/$3.00

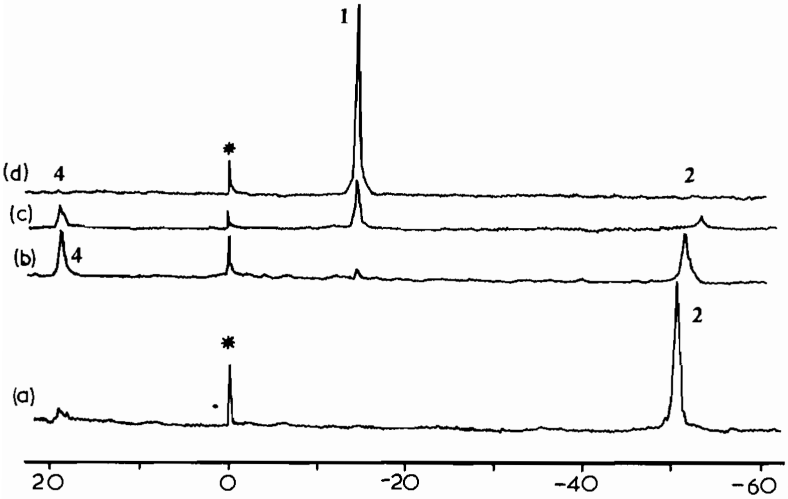


Fig. 1. ^{31}P NMR spectra of the reaction mixture obtained by treating complex **2** with CO/H_2O at times: (a) 0, (b) 1 h, (c) 4 h, (d) 15 h. The numbers **1**, **2**, **4**, refer to the peaks due to those complexes. A peak due to complex **3** is observed at intermediate stages if the CO pressure is reduced, and the peak labelled asterisk is due to the reference trimethyl phosphate.

tainly the rate-determining step, the overall rate of cluster formation is also faster starting from **2** than from **3**. The palladium(0) intermediate is represented as Pd(dppm) or $Pd_2(dppm)_2$ in the Scheme, but it is too shortlived to be observed directly, and would probably also contain co-ordinated CO for additional stabilization. The final step proposed in the formation of **1**, involves displacement of $CF_3CO_2^-$ ligands from **4** by the Pd·(dppm) species. and this is also aided by the good leaving group, $CF_3CO_2^-$

As a further check on the proposed mechanism, the reductions of 2 and 3 with the stable palladium(0) complex $[Pd_2(\mu\text{-dppm})_3]$ have been studied [6] (eqn. 3, $X = CF_3CO_2$). These reactions are rapid and lead to formation of **1**, as expected. However, the excess dppm causes some disproportionation to give the unreactive $[Pd(dppm)_2]^{2+}$ ion as the trifluoroacetate salt. Again, the reactions were monitored by ^{31}P NMR spectroscopy.*

$$\begin{aligned}&[PdX_2(dppm)] + [Pd_2(dppm)_3] \longrightarrow\\ &\qquad\qquad [Pd_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]X_2\\ &\qquad\qquad\nearrow\\ &[Pd_2X_2(dppm)_2] + \tfrac{1}{2}[Pd_2(dppm)_3] \qquad (3)\end{aligned}$$

In conclusion, these results show that reduction of complex **2** to the cluster **1** by CO/H_2O involves reduction to a Pd·(dppm) species which, in turn reacts with mononuclear **2** to give the dinuclar complex **3** and then with dinuclear **4** to give the final trinuclear cluster **1**.

Acknowledgement

We thank NSERC (Canada) for financial support.

References

1 D. A. Roberts and G. L. Geoffrey, in E. W. Abel, F. G. A. Stone and G. Wilkinson, (eds.), 'Comprehensive Organometallic Chemistry', Pergamon, Oxford, 1972, ch. 40.
2 P. M. Maitlis, P. Espinet and M. J. H. Russel, in E. W. Abel, F. G. A. Stone and G. Wilkinson (eds.), 'Comprehensive Organometallic Chemistry', Pergamon, Oxford, 1982, ch. 38.3.
3 Lj. Manojlovic-Muir, K. W. Muir, B. R. Lloyd and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1336 (1983).
4 L. S. Benner and A. L. Balch, *J. Am. Chem. Soc., 100,* 6099 (1978).
5 P. Chini and G. Longoni, *J. Am. Chem. Soc., 98,* 7225 (1976).
6 C. T. Hunt and A. L. Balch, *Inorg. Chem., 20,* 2267 (1981).

---

*See footnote page L77.