Deactivation of a [PPN][Rh(CO)$_4$]-based catalytic system [PPN$^+$ = (PPh$_3$)$_2$N$^+$]. The first decomposition reaction of PPN$^+$ and the formation of [Rh$_{10}$P(CO)$_{22}$]$^{3-}$†

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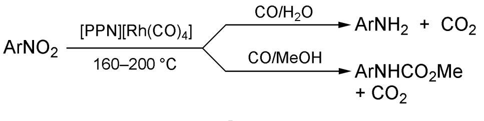
Decomposition of [PPN][Rh(CO)$_4$] [PPN$^+$ = (PPh$_3$)$_2$N$^+$] at 200 °C under CO pressure affords [Rh$_{10}$P(CO)$_{22}$]$^{3-}$, featuring the first decomposition reaction of PPN$^+$ and explaining the reason for the deactivation of [PPN][Rh(CO)$_4$]-based catalytic systems.

Tetraalkyl and aryl ammonium and phosphonium cations are widely used to improve isolability and solubility of anionic organometallic complexes in organic solvents. However, they usually suffer from limited chemical stability, especially in basic media. In contrast, the PPN$^+$ cation [PPN$^+$ = (PPh$_3$)$_2$N$^+$], first isolated by Appel,[1] is generally considered as a chemically very stable and little interacting counter cation. For these reasons, it has found an increasingly important use in organometallic chemistry and homogeneous catalysis. Although the 'non-interacting' character of PPN$^+$ has later been questioned,[2] to the best of our knowledge its chemical stability is still undisputed.

In recent years, some of us have been involved in the use of [PPN][Rh(CO)$_4$] as a catalyst for the reduction reactions of nitroarenes by CO/MeOH[3] or CO/H$_2$O[4] to afford respectively methyl arylcarbamates (ArNHCO$_2$Me) or anilines (Scheme 1).



Scheme 1

Despite the high catalytic activity of [PPN][Rh(CO)$_4$] in these reactions, deactivation of the catalytic system was observed upon prolonged use. We thus decided to investigate the fate of rhodium in these reactions. Since the products of reduction and carbonylation of nitroarenes are difficult to separate from the small amounts of catalyst-derived complexes, we examined the behaviour of [PPN][Rh(CO)$_4$] under similar experimental conditions, but in the absence of any nitroarene.

Heating [PPN][Rh(CO)$_4$] in acetone–water (instead of nitrobenzene–water) at 200 °C and under 60 bar CO for 4 h afforded a brown precipitate. Only very weak carbonyl bands were observed in the IR spectrum of the solution. The IR spectrum of the residue dissolved in CH$_2$Cl$_2$ showed a strong band at 1990 cm^{-1} (in CH$_2$Cl$_2$), with several shoulders, and a series of overlapping bands between 1840 and 1775 cm^{-1}. No [Rh(CO)$_4$]$^-$ was detected either in solution or in the solid residue.

When this last residue was used in place of [PPN][Rh(CO)$_4$] as catalyst for the reduction of nitrobenzene to aniline,[4] only trace amounts of the amine were obtained, indicating that the formed compound(s) is catalytically inactive.

Recrystallisation of the residue from acetonitrile + acetone (1 : 1)–diisopropyl ether afforded crystals of a cluster that was identified by single-crystal X-ray diffraction as [PPN]$_3$[Rh$_{10}$P(CO)$_{22}$],‡ having an interstitial phosphorus atom. [PPN]$_3$[Rh$_{10}$P(CO)$_{22}$] crystallises in the centrosymmetric triclinic space group $P\bar{1}$ with two independent (half) [Rh$_{10}$P(CO)$_{22}$]$^{3-}$ anions disordered about two distinct centres of symmetry. Two independent PPN cations are in general position while the third one consists of two (ordered, independent) halves lying about two distinct centres of symmetry. The [Rh$_{10}$P(CO)$_{22}$]$^{3-}$ anion which has a bicapped square antiprismatic metal core (see Fig. 1) has been previously structurally characterised as a triethylbenzylammonium salt[5] but, owing to the intrinsic centrosymmetric nature of its ligand envelope (all the external oxygen atoms were actually ordered), suffered of a similar disorder. The present, more accurate, structure determination confirms most of the previous stereochemical observations but also shows the marked effect of different packing environments by comparing the actual values of the distances, and their averages, in the three independent anions (Table 1, ESI†).

The identification of a cluster species having an interstitial phosphorus atom is very informative, since this atom can only derive from decomposition of the PPN$^+$ counter cation. The

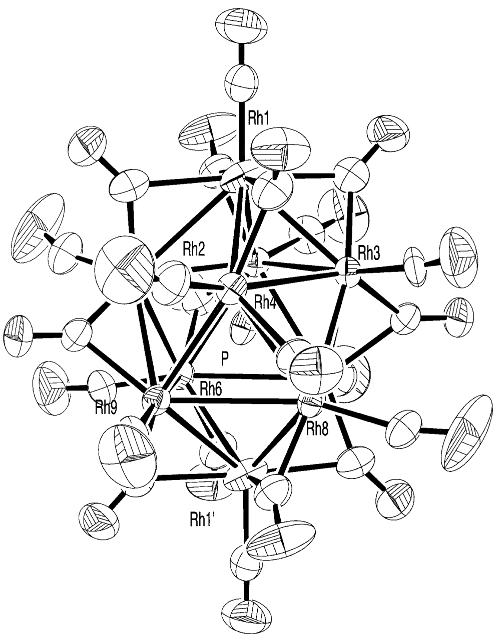


Fig. 1 ORTEP drawing of the [Rh$_{10}$P(CO)$_{22}$]$^{3-}$ anion (B). Thermal ellipsoids are drawn at the 50% probability level.

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† Electronic supplementary information (ESI) available: Table 1: selected bond lengths (Å) for [PPN][Rh$_{10}$P(CO)$_{22}$]. See http://www.rsc.org/suppdata/cc/b0/b006135m/

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decomposition must be initiated by a rhodium complex, since no acids or bases are present in the reaction mixture. To the best of our knowledge, this is the first time a decomposition product of PPN$^+$ is identified. The formation of $[Rh_{10}P(CO)_{22}]^{3-}$ also explains the loss of activity of the catalytic system. Indeed, whereas many rhodium clusters are known to convert to mononuclear species under high CO or CO/H_2 pressures,[6] this phosphido cluster has been shown to be remarkably stable even under CO/H_2 pressures much higher than that used both in our studies and in most of those from other laboratories.[5] The formation of $[Rh_{10}P(CO)_{22}]^{3-}$ must thus be considered as irreversible in most if not all catalytic systems and represents a warning against the use of PPN$^+$ as a counter cation when very long catalyst lives are required, as in industrial applications.

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Notes and references

‡ *X-Ray crystallography*: the diffraction experiment was performed using a suitable crystal (of dimensions 0.23 × 0.17 × 0.15 mm), on a Siemens SMART CCD area-detector diffractometer, by measuring 2100 frames (20 s per frame; ω scan method, $\Delta\omega = 0.3°$; sample-detector distance fixed at 5 cm) which, upon data reduction, afforded almost all reflections belonging to the sphere with $2\theta < 55°$. The first 100 frames were recollected at the end to monitor crystal decay, which was not observed; an absorption correction was applied (SADABS).[7] The structure was solved by direct methods (SIR97)[8] and refined with full-matrix least squares (SHELX97);[9] anisotropic temperature factors were assigned to all atoms except phenyl hydrogens which were allowed to ride on their carbon atoms with individual isotropic displacement parameters 1.2 times that of the pertinent carbon atom. Data/restraints/parameters 24974/55/1702, GOF (on F^2) = 0.983; $R = 0.0372$, $wR2 = 0.0767$, for $I > 2\sigma(I)$, $R = 0.0705$, $wR2 = 0.0886$, for all data; largest difference peak and hole 0.95 and −1.06 e Å^3.

Crystal data: $C_{130}H_{90}N_3O_{22}P_7Rh_{10}$, $M = 3291.94$, triclinic, space group $P\bar{1}$, $a = 16.2084(7)$, $b = 16.3039(7)$, $c = 23.9367(11)$ Å, $\alpha = 91.241(1)$, $\beta = 94.880(1)$, $\gamma = 90.067(1)°$, $U = 6301.1(5)$ Å^3, $Z = 2$, $D_c = 1.735$ Mg m^{-3}, $T = 298(2)$ K, μ(Mo-Kα) = 1.431 mm^{-1}, $F(000) = 3244$. 66631 Reflections collected 24974 unique ($R_{int} = 0.0432$).

CCDC 182/1784. See http://www.rsc.org/suppdata/cc/b0/b006135m/ for crystallographic files in .cif format.

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