

such redox series are known for these and other elements.

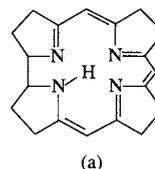
26.3.4 The biochemistry of cobalt⁽³⁴⁾

The wasting disease in sheep and cattle known variously as “pine” (Britain), “bush sickness” (New Zealand), “coast disease” (Australia), and “salt sick” (Florida) has been recognized since the late eighteenth century. When it was realized to be an anaemic condition it was thought to be due to iron deficiency and was therefore treated, with mixed success, by administering iron salts. Then, in the 1930s, it was found by workers in Australia and New Zealand that the efficacious principle in the iron treatment was actually an impurity (cobalt) but its role was not understood. This became more evident when vitamin B₁₂ was extracted from raw liver and shown to be responsible for the latter’s well-known effectiveness in treating pernicious anaemia. It is now known that vitamin B₁₂ is a coenzyme[†] in a number of biochemical processes, the most important of which is the formation of erythrocytes (red blood-cells). It obviously functions extremely effectively, the human body for instance containing a mere 2–5 mg, concentrated in the liver.

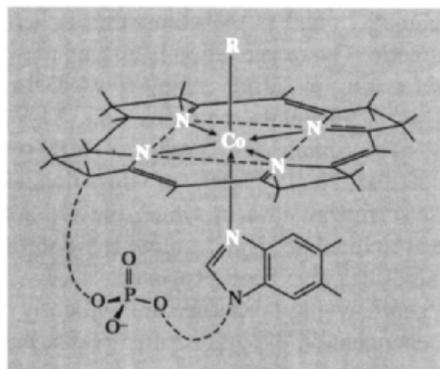
The structure of the diamagnetic, cherry-red vitamin B₁₂ is shown in Fig. 26.6 and it can be seen that the coordination sphere of the cobalt has many similarities with that of iron in haem (see Fig. 25.7). In both cases the metal is coordinated to 4 nitrogen atoms of an unsaturated macrocycle (in this case part of a “corrin” ring which is less symmetrical and not so unsaturated as the porphyrin in haem) with an imidazole nitrogen in the fifth position. A major

³⁴ W. KAIM and B. SCHWERDESKI, pp. 39–55 of *Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life*, Wiley, Chichester, 1994; L. R. MILGROM, *Chem. in Brit.* **31**, 923–7 (1994).

[†] Enzymes are proteins which act as very specific catalysts in biological systems. Their activity may depend on the presence of substances, often metal complexes, of much lower molecular weight. These activators are known as “coenzymes”.

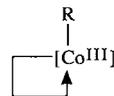


(a)



(b)

Figure 26.6 Vitamin B₁₂: (a) a corrin ring showing a square-planar set of N atoms and a replaceable H, and (b) simplified structure of B₁₂. In view of the H displaced from the corrin ring, the Co–C bond, and the charge on the ribose phosphate, the cobalt is formally in the +3 oxidation state. This and related molecules are conveniently represented as:



difference is apparent, however, in the sixth coordination position which, in haemoglobin, is either vacant or occupied by O₂. Here it is filled by a σ -bonded carbon,⁽³⁵⁾ making vitamin B₁₂ the first, and so far the only, fully established naturally occurring organometallic compound. The usual methods of isolation lead to a product known as *cyanocobalamin*, which is the same as vitamin B₁₂ itself but with CN[−] instead of deoxyadenosine in the sixth coordination position. This is a labile site, and other derivatives such as *aquocobalamin* can be prepared.

Incorporation of cobalt into the corrin ring system modifies the reduction potentials of

³⁵ D. C. HODGKIN, *Proc. Roy. Soc. A* **288**, 294–305 (1965).

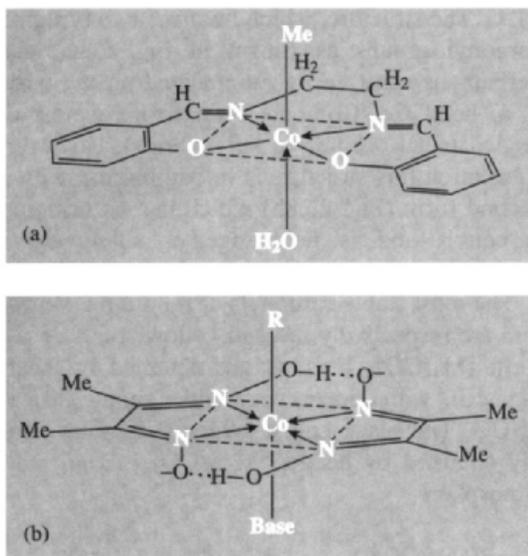
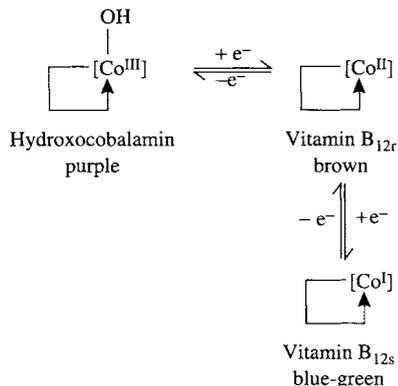


Figure 26.7 Model vitamin B₁₂ compounds: (a) a Schiff base derivative, and (b) a cobaloxime, in this case derived from dimethylglyoxime.

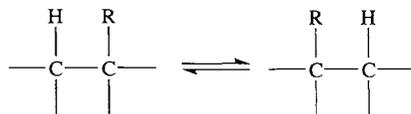
cobalt giving it three accessible and consecutive oxidation states:



The reductions are effected in nature by ferredoxin (p. 1102). This behaviour can be reproduced surprisingly well by simpler, model compounds. Some of the best known of these are obtained by the addition of axial groups to the square-planar complexes of Co^{II} with Schiff bases, or substituted glyoximes (giving cobaloximes) as illustrated in Fig. 26.7. The reduced Co^I species of these, along with vitamin

B_{12s}, are amongst the most powerful nucleophiles known (hence, “supernucleophiles”), liberating H₂ from water.

Virtually all the biological processes, in which vitamin B₁₂ is active, involve substituent exchange of the type:



which, significantly, does not involve solvent protons. The precise mechanism of these reactions is not settled but all involve cleavage of the Co–C bond and it is evident from the study of model systems that the lack of complete planarity of the corrin ring is an important factor in controlling this.⁽³⁶⁾

26.3.5 Organometallic compounds⁽³⁷⁾

Many of the organometallic compounds of the elements of this group show valuable catalytic activity and, as discussed above, much of the chemistry of vitamin B₁₂ is the chemistry of the Co–Cσ bond. Simple homoleptic alkyls and aryls of cobalt, [CoR_x], have not in fact been prepared, but this is evidently not due to thermodynamic instability of the Co–C bond. Compounds containing such bonds can be prepared in abundance, not only with (σ + π)-bonding ligands such as phosphines and CO but also with non-π-bonding ligands such as Schiff bases and glyoximes. These latter presumably owe their existence not to electronic but rather to steric factors, the additional ligands blocking what might otherwise be energetically favourable decomposition paths.

³⁶ M. RAVIKANTH and T. K. CHANRESHEKAR, *Structure and Bonding*, **82**, 105–88 (1995).

³⁷ R. S. DICKSON, *Organometallic Chemistry of Rhodium and Iridium*, Academic Press, New York, 1983, 432 pp.; C. WHITE, *Organometallic Compounds of Cobalt, Rhodium and Iridium*, Chapman & Hall, London 1985, 296 pp.

Carbonyls (see p. 926)

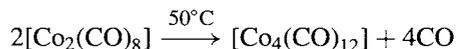
Because they possess an odd number of valence electrons the elements of this group can only satisfy the 18-electron rule in their carbonyls if M–M bonds are present. In accord with this, mononuclear carbonyls are not formed. Instead $[M_2(CO)_8]$, $[M_4(CO)_{12}]$ and $[M_6(CO)_{16}]$ are the principal binary carbonyls of these elements. But reduction of $[Co_2(CO)_8]$ with, for instance, sodium amalgam in benzene yields the monomeric and tetrahedral, 18-electron ion, $[Co(CO)_4]^-$, acidification of which gives the pale yellow hydride, $[HCo(CO)_4]$. Reductions employing Na metal in liquid NH_3 yield the "super-reduced" $[M(CO)_3]^{3-}$ (M = Co, Rh, Ir) containing these elements in their lowest formal oxidation state.⁽³⁸⁾

The importance of cobalt carbonyls lies in their involvement in hydroformylation reactions discussed above. The original, and still widely used, process depends on the use of cobalt salts rather than the newer rhodium catalysts (pp. 1134–5). The mechanism of the cobalt cycle is more difficult to ascertain but it seems clear that the active agent is the hydride, $[HCo(CO)_4]$. It is, moreover, plausible that the cycle is basically the same as that outlined in Fig. 26.5 but starting with loss of CO from $[HCo(CO)_4]$ rather than loss of phosphine from $[Rh(CO)H(PPh_3)_3]$, so producing a comparable coordinatively unsaturated intermediate to which the alkene can attach itself. The disadvantages of the system, as already mentioned, are its lack of specificity, leading to branched-chain products, and the necessity of high temperatures ($>150^\circ C$) and pressure (~ 200 atm). In addition the volatility of $[HCo(CO)_4]$ poses recovery problems.

The dinuclear octacarbonyls are obtained by heating the metal (or in the case of iridium, $IrCl_3$ + copper metal) under a high pressure of CO (200–300 atm). $Co_2(CO)_8$ is by far the best known, the other two being poorly characterized; it is an air-sensitive, orange-red solid melting at

$51^\circ C$. The structure, which involves two bridging carbonyl groups as shown in Fig. 26.8a, can perhaps be most easily rationalized on the basis of a "bent" Co–Co bond arising from overlap of angled metal orbitals (d^2sp^3 hybrids). However, in solution this structure is in equilibrium with a second form (Fig. 26.8b) which has no bridging carbonyls and is held together solely by a Co–Co bond.

The most stable carbonyls of rhodium and iridium are respectively red and yellow solids of the form $[M_4(CO)_{12}]$ which are obtained by heating MCl_3 with copper metal under about 200 atm of CO. The black cobalt analogue is more simply obtained by heating $[Co_2(CO)_8]$ in an inert atmosphere



The structures are shown in Fig. 26.8c and d and differ in that, whereas the Ir compound consists of a tetrahedron of metal atoms held together solely by M–M bonds, the Rh and Co compounds each incorporate 3 bridging carbonyls. A similar difference was noted in the case of the trinuclear carbonyls of Fe, Ru and Os (p. 1104) and can be explained in a similar way.⁽³⁹⁾ The M_4 tetrahedra of Co and Rh are small enough to be accommodated in an icosahedral array of CO ligands whereas the larger Ir_4 tetrahedron forces the adoption of the less dense cube octahedral array of ligands.

Of the $[M_6(CO)_{16}]$ carbonyls the very dark-brown Rh compound prepared simultaneously with and separated from $[Rh_4(CO)_{12}]$ is the best known. In the solid its structure consists of an octahedral array of $Rh(CO)_2$ units with the remaining 4 CO's bridging 4 faces of the octahedron (Fig. 26.8e). A black isomorphous, and presumably isostructural, Co analogue and an isostructural red Ir analogue are known. A second, black Ir isomer occurs which differs only in that it has 4 edge-bridging rather than face-bridging CO groups. Again rationalization is possible on the basis of the ligand polyhedral

³⁸ J. E. ELLIS, *Adv. Organometallic Chem.*, **31**, 1–52 (1990).

³⁹ B. F. G. JOHNSON and Y. V. ROBERTS, *Polyhedron*, **12**, 977–90 (1993).

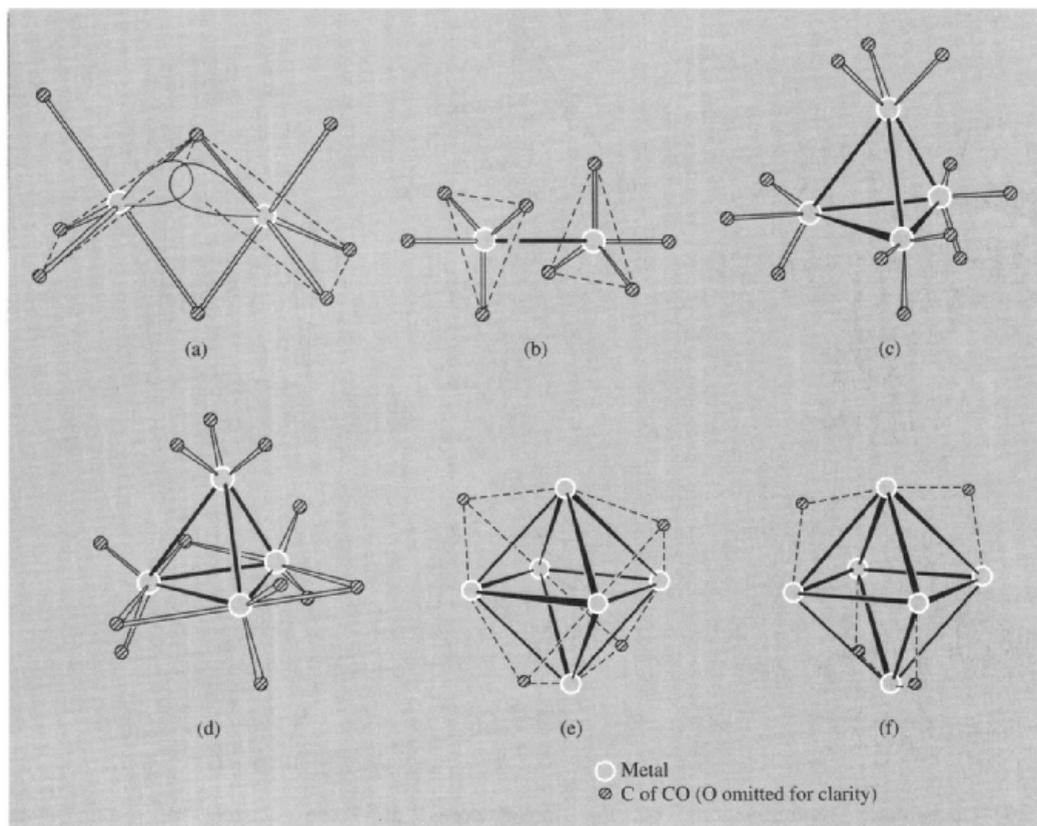


Figure 26.8 Molecular structures of some binary carbonyls of Co, Rh, and Ir. (a) $\text{Co}_2(\text{CO})_8$ in solid state, showing the formation of a “bent” Co–Co bond. (b) $\text{Co}_2(\text{CO})_8$ in solution. (c) $\text{Ir}_4(\text{CO})_{12}$. (d) $\text{M}_4(\text{CO})_{12}$, $\text{M} = \text{Co}, \text{Rh}$. (e) $\text{M}_6(\text{CO})_{16}$ $\text{M} = \text{Co}, \text{Rh}$ and Ir (for its red isomer). (f) black isomer of $\text{Ir}_6(\text{CO})_{16}$.

model. In *both* structures the ligands occupy the 16 vertices of a tetracapped truncated tetrahedron. In one case the 4 caps are the face-bridging ligands, in the other the edge-bridging ligands. The two structures are related by a simple rotation of the M_6 octahedron about a C_4 axis.⁽³⁹⁾

Carbonyl hydrides and carbonylate anions are obtained by reducing neutral carbonyls, as mentioned above, and in addition to mononuclear metal anions, anionic species of very high nuclearity have been obtained, often by thermolysis. These are especially numerous for Rh and in certain Rh_{13} , Rh_{14} and Rh_{15} anions have structures conveniently visualized either as polyhedra encapsulating further metal atoms, or alternatively as arrays of metal atoms forming portions of hexagonal close packed or body

centred cubic lattices stabilized by CO ligands. $[\text{Rh}_{13}\text{H}_3(\text{CO})_{24}]^{2-}$ (Fig 26.9a) is typical.

The anionic cluster $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ is octahedral and an increasing number of Ir clusters have been reported recently though their preparations are more difficult and yields usually smaller than for rhodium. $[\text{Ir}_{14}(\text{CO})_{27}]^-$ has the highest nuclearity so far and is obtained as black crystals by oxidizing $[\text{Ir}_6(\text{CO})_{15}]^{2-}$ with ferricinium ion⁽⁴⁰⁾ (Fig 26.9b).

The incorporation of interstitial or encapsulated heteroatoms is a common and stabilizing feature. Carbon is the most common and, as is the case in

⁴⁰ R. D. PERGOLA, L. GARLASCELLI, M. MANASSERO, N. MASCIOCCHI and P. ZANELLO, *Angew. Chem. Int. Edn. Engl.* **32**, 1347–9 (1993).

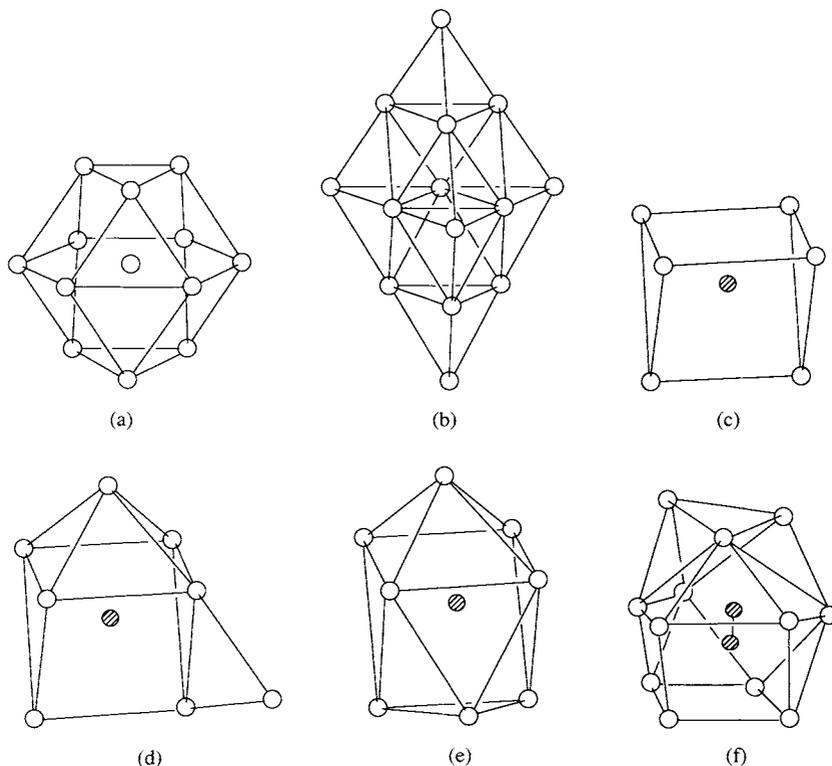


Figure 26.9 Schematic representations of the metal cores of some clusters of group 9 metals. (a) $[\text{Rh}_{13}\text{H}_3(\text{CO})_{24}]^{2-}$; the H atoms migrate within the cluster. (b) $[\text{Ir}_{14}(\text{CO})_{27}]^-$. (c) $[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$. (d) $[\text{Rh}_8\text{C}(\text{CO})_{19}]$; a trigonal prism of 6 Rh atoms has one face capped by a seventh Rh atom and one edge bridged by the eighth Rh atom. (e) $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$; the 8 Co atoms define a distorted bicapped trigonal prism which, alternatively, can be viewed as a distorted square antiprism. (f) $[\text{Rh}_{12}(\text{C}_2)(\text{CO})_{25}]$.

group 8 (p. 1107), may originate from the solvent or from cleavage of a CO ligand. The carbido C contributes 4 electrons to the cluster bonding and in the 90-electron species $[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}$ features trigonal prismatic coordination of Rh_6 about the central C (Fig. 26.9c). More complex geometries are found for $[\text{Rh}_8\text{C}(\text{CO})_{19}]$ (Fig. 26.9d) and $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$ (Fig. 26.9e): these two iso-electronic clusters are not isostructural though a slight distortion would (hypothetically) transform one into the other. The central carbido C in the square antiprismatic $[\text{Co}_8\text{C}(\text{CO})_{18}]^{2-}$ is formally 8-coordinate, the Co–C distances being in the range 195–220 pm with a mean value of 207 pm. Even more complicated structures are found for the large Rh clusters containing 2 carbido

C atoms: $[\text{Rh}_{12}(\text{C}_2)(\text{CO})_{25}]$ (Fig. 26.9f has no symmetry elements but it is clear that the Rh_{12} cluster surrounds an ethanide unit C_2 in which the C–C distance is only 147 pm); the cluster also has 14 pendant terminal CO groups, 10 μ -CO groups and one μ_3 -CO. In contrast, $[\text{Rh}_{15}(\text{C})_2(\text{CO})_{28}]^-$ has individual 6-coordinate (octahedral) carbido C atoms symmetrically placed on each side of a central Rh which itself has 12 Rh nearest neighbours in addition to the 2 C atoms. Again, the approach to metal structures is notable and is one of the main interests in constructing large clusters and studying their chemical and catalytic activity.

H, P, As, S have also been encapsulated in ions such as $[\text{Rh}_{13}(\text{H})_3(\text{CO})_{24}]^{2-}$, $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$, $[\text{Rh}_{10}\text{As}(\text{CO})_{22}]^{3-}$ and $[\text{Rh}_{17}(\text{S})_2(\text{CO})_{32}]^{3-}$.

More recently N has been encapsulated⁽⁴¹⁾ in $[\text{Rh}_{14}(\text{N})_2(\text{CO})_{25}]^{2-}$ and $[\text{Rh}_{23}(\text{N})_4(\text{CO})_{38}]^{3-}$. The latter is the largest Rh cluster so far characterized. It consists of an irregular polyhedron of 21 Rh atoms encapsulating a pair of particularly close (257.1 pm) Rh atoms as well as 4 N atoms each of which is located in a semi octahedral site.

Other derivatives of the carbonyls are of course numerous; Ir forms many carbonyl halides of the types $[\text{Ir}^{\text{I}}(\text{CO})_3\text{X}]$, $[\text{Ir}^{\text{I}}(\text{CO})_2\text{X}_2]^-$, $[\text{Ir}^{\text{III}}(\text{CO})_2\text{X}_4]^-$ and $[\text{Ir}^{\text{III}}(\text{CO})\text{X}_5]^{2-}$, but the stability of carbonyl halides falls off in the sequence $\text{Ir} > \text{Rh} > \text{Co}$ and those of Co are only of the type $[\text{Co}(\text{CO})_4\text{X}]$ and are very unstable.

The bulk of derivatives are obtained by the displacement of CO by other ligands. These include phosphines and other group 15 donors, NO, mercaptans and unsaturated organic molecules such as alkenes, alkynes and cyclopentadienyls.

Cyclopentadienyls

Cobaltocene, $[\text{Co}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$, is a dark-purple air-sensitive material, prepared by the reactions of sodium cyclopentadiene and anhydrous CoCl_2

in thf. Having 1 more electron than ferrocene, it is paramagnetic with a magnetic moment of 1.76 BM and, while it is thermally stable up to 250°C, its most obvious characteristic is its ready loss of this electron to form the yellow-green cobalticenium ion, $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_5)_2]^+$. This resists further oxidation, being stable even in conc HNO_3 but, like the isoelectronic ferrocene, is susceptible to nucleophilic attack on its rings.

Rhodocene, $[\text{Rh}(\eta^5\text{-C}_5\text{H}_5)_2]$, is also known but is unstable to oxidation and has a tendency to form dimeric species. Claims for the existence of iridocene probably refer to Ir^{III} complexes. However, the yellow rhodicenium and iridicenium cations are certainly known and are entirely analogous to the cobalticenium cation in their resistance to oxidation and susceptibility to nucleophilic attack.

Numerous "half-sandwich" compounds of the type $[\text{M}(\eta^5\text{-C}_5\text{R}_5)\text{L}_2]$, $\text{M} = \text{Rh}, \text{Ir}$; $\text{R} = \text{H}, \text{Me}$; $\text{L} = \text{CO}, \text{phosphine}$ etc.) are known and are useful reagents. $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ for instance is an excellent nucleophile and is also used in the photochemical activation of C-H in alkanes. It is particularly effective in the latter role when supercritical CO_2 is the solvent.⁽⁴²⁾

⁴¹ S. MARTINENGO, G. CIANI and A. SIRONI, *J. Chem. Soc., Chem. Commun.*, 1405-6 (1992).

⁴² M. JOBLING, S. M. HOWDLE, M. A. HEALY and M. POLIAKOFF, *J. Chem. Soc., Chem. Commun.*, 1287-90 (1990).