no reason to doubt that this is true for Ni^0. For Pd^0 and Pt^0, however, it appears that σ-bonding ability is also important, and the smaller importance of π backbonding which this implies is in accord with the higher ionization energies of Pd and Pt [804 and 865 kJ mol^{-1} respectively] compared with that for Ni [737 kJ mol^{-1}].

27.3.5 The biochemistry of nickel[27]

Until the discovery in 1975 of nickel in jack bean urease (which, 50 years previously, had been the first enzyme to be isolated in crystalline form and was thought to be metal-free) no biological role for nickel was known. Ureases occur in a wide variety of bacteria and plants, catalyzing the hydrolysis of urea,

$$OC(NH_2)_2 + H_2O \longrightarrow H_2NCOO^- + NH_4{}^+$$
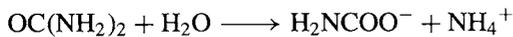
Results from an array of methods, including X-ray absorption, EXAFS, esr and magnetic circular dichroism, suggest that in all ureases the active sites are a pair of Ni^{II} atoms. In at least one urease,[27a] these are 350 pm apart and are bridged by a carboxylate group. One nickel is attached to 2 N atoms with a fourth site probably used for binding to urea. The second nickel has a trigonal bipyramidal coordination sphere.

Three other Ni-containing enzymes found in bacteria have now been identified:
Hydrogenases, most of which also contain Fe and catalyse the reaction, $2H_2 + O_2 \longrightarrow 2H_2O$. The Ni has a coordination sphere of 5 or 6 mixed *S-*, *N-*, *O-*donors and is believed to undergo redox cycling between III, II and I oxidation states.
CO Dehydrogenase, also incorporating Fe and catalysing the oxidation of CO to CO_2. The attachment of CO to a nickel centre coordinated to perhaps four *S*-donors is postulated.

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[27] A. F. KOLODZIEJ, *Prog. Inorg. Chem.* **41**, 493–597 (1994); J. R. LANCASTER (ed.), *The Bioinorganic Chemistry of Nickel*, VCH, Weinheim, 1988, 337 pp.; H. SIGEL (ed.), *Metal Ions in Biological Systems*, Vol. 23, *Nickel and its Role in Biology*, Dekker, New York, 1988, 488 pp.

[27a] S. J. LIPPARD, *Science*, **268**, 996–7 (1995); E. JABRI, M. B. CARR, R. P. HAUSINGER and P. A. KARPLUS, *ibid.* pp. 998–1004.

Methyl-coenzyme M reductase participates in the conversion of CO_2 to CH_4 and contains 6-coordinate nickel(II) in a highly hydrogenated and highly flexible porphyrin system. This flexibility is believed to allow sufficient distortion of the octahedral ligand field to produce low-spin Ni^{II} (Fig. 27.7) which facilitates the formation of a Ni^I–CH_3 intermediate.

27.3.6 Organometallic compounds[4,28]

All three of these metals have played major roles in the development of organometallic chemistry. The first compound containing an unsaturated hydrocarbon attached to a metal (and, indeed, the first organometallic compound if one excludes the cyanides) was $[Pt(C_2H_4)Cl_2]_2$, discovered by the Danish chemist W. C. Zeise as long ago as 1827 and followed 4 years later by the salt which bears his name, $K[Pt(C_2H_4)Cl_3].H_2O$. $[Ni(CO)_4]$ was the first metal carbonyl to be prepared when L. Mond and his co-workers discovered it in 1888. The platinum methyls, prepared in 1907 by W. J. Pope, were amongst the first-known transition metal alkyls, and the discovery by W. Reppe in 1940 that Ni^{II} complexes catalyse the cyclic oligomerization of acetylenes produced a surge of interest which was reinforced by the discovery in 1960 of the π-allylic complexes of which those of Pd^{II} are by far the most numerous.

σ-Bonded compounds

These are of two main types: compounds of M^{IV}, which for platinum have been known since the beginning of this century and commonly involve the stable {PtMe_3} group; and compounds of the divalent metals, which were first studied by J. Chatt and co-workers in the late 1950's and are commonly of the type $[MR_2L_2]$ (L = phosphine). In the Pt^{IV} compounds the metal is always octahedrally coordinated and this is frequently achieved in interesting ways. Thus the trimethyl halides, conveniently obtained

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[28] G. WILKE, *Angew. Chem. Int. Edn. Engl.* **27**, 185–206 (1988).

by treating $PtCl_4$ with MeMgX in benzene, are tetramers, $[PtMe_3X]_4$, in which the 4 Pt atoms form a cube involving triply-bridging halogen atoms[†] (Fig. 27.11a). The dimeric $[PtMe_3(acac)]_2$ is also unusual in that the acac is both *O*- and *C*-bonded (Fig. 27.11b), while in $[PtMe_3(acac)(bipy)]$ 7-coordination is avoided because the acac coordinates merely as a unidentate *C*-donor. Pd^{IV} compounds such as $[PdI(bipy)Me_3]$ are also octahedral but are limited in number and much less stable than those of Pt^{IV}, being susceptible to reductive elimination.[(29)]

[†] The chequered history of compounds of this type makes salutory reading. H. Gilman and M. Lichtenwalter (1938, 1953) reported the synthesis of $PtMe_4$ in 46% yield by reacting Me_3PtI with NaMe in hexane. R. E. Rundle and J. H. Sturdivant determined the X-ray crystal structure of this product in 1947 and described it as a tetramer $[(PtMe_4)_4]$: this required the concept of a multicentred, 2-electron bond, and was one of the first attempts to interpret the bonding in a presumed electron-deficient cluster compound. In fact, tetramethylplatinum cannot be prepared in this way and is unknown; Gilman's compound was actually a hydrolysis product $[\{PtMe_3(OH)\}_4]$ and the mistaken identity of the crystal went undetected by the X-ray work because, at that time, the scattering curves for the 9-electron groups CH_3 and OH were indistinguishable in the presence of Pt. Interestingly, the compound $PtMe_3(OH)$ had, in reality, already been synthesized by W. J. Pope and S. J. Peachey as long ago as 1909, and its tetrameric structure was confirmed by subsequent X-ray work.[(30)] In a parallel study,[(31)] the transparent tan-coloured tetramer $[(PtMe_3I)_4]$ has now been shown to be the same compound as was previously erroneously reported in 1938 as hexamethyldiplatinum, $[Me_3Pt–PtMe_3]$. This was equally erroneously described in 1949 on the basis of an incomplete X-ray structural study as a methyl-bridged oligomer $[(PtMe_3)_{12}]$ or an infinite chain of methyl-bridged 6-coordinate $\{PtMe_3\}$-groups. A qualitative test for iodine would have revealed the error 30 years earlier.

Although $PtMe_4$ remains unknown it has more recently been shown that reaction of $[PtMe_2(PPh_3)_2]$ with LiMe yields the square-planar Pt^{II} complex $Li_2[PtMe_4]$, whereas reaction of $[PtMe_3I]_4$ with LiMe affords the octahedral Pt^{IV} complex $Li_2[PtMe_6]$.[(32)] The thermally stable, colourless, 8-coordinate complex $[PtMe_3(\eta^5\text{-}C_5H_5)]$ is also known.[(33)]

[29] A. J. CANTY, *Acc. Chem. Res.* **25**, 83–90 (1992); *Platinum Metals Rev.* **37**, 2–7 (1993).

[30] D. O. COWAN, N. G. KRIEGHOFF and G. DONNAY, *Acta Cryst.* **B24**, 287–8 (1968), and references therein.

[31] G. DONNAY, L. B. COLEMAN, N. G. KRIEGHOFF and D. O. COWAN, *Acta Cryst.* **B24**, 157–9 (1968), and references therein.

[32] G. W. RICE and R. S. TOBIAS, *J. Am. Chem. Soc.* **99**, 2141–9 (1977).

[33] O. HACKELBERG and A. WOJCICKI, *Inorg. Chim. Acta* **44**, L63–L64 (1980).

○ Platinum
○ Chlorine
● Carbon of Me   ○ Oxygen of acac
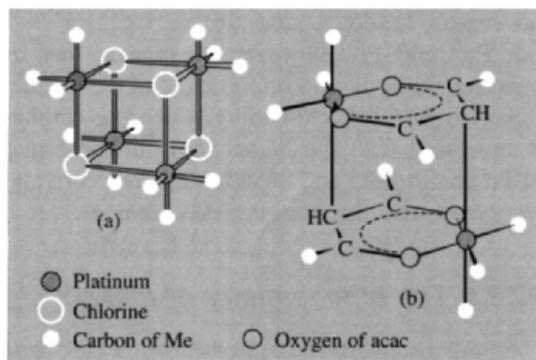
Figure 27.11   Schematic representation of the structures of compounds containing octahedrally coordinated Pt^{IV}:
(a) the tetramer, $[PtMe_3Cl]_4$, and
(b) the dimer, $[PtMe_3(acac)]_2$.

The stabilities of the $[ML_2R_2]$ phosphines increase from Ni^{II} to Pt^{II} and for Ni^{II} they are only isolable when R is an *o*-substituted aryl. Those of Pt^{II}, on the other hand, are amongst the most stable σ-bonded organo-transition metal compounds while those of Pd^{II} occupy an intermediate position.

Carbonyls (see p. 926)

On the basis of the 18-electron rule, the d^8s^2 configuration is expected to lead to carbonyls of formula $[M(CO)_4]$ and this is found for nickel. $[Ni(CO)_4]$, the first metal carbonyl to be discovered, is an extremely toxic, colourless liquid (mp $-19.3°$, bp $42.2°$) which is tetrahedral in the vapour and in the solid (Ni–C 184 pm, C–O 115 pm). Its importance in the Mond process for manufacturing nickel metal has already been mentioned as has the absence of stable analogues of Pd and Pt. It may be germane to add that the introduction of halides (which are σ-bonded) reverses the situation: $[NiX(CO)_3]^-$ (X = Cl, Br, I) are very unstable, the yellow $[Pd^{II}(CO)Cl_2]_n$ is somewhat less so, whereas the colourless $[Pt^{II}(CO)_2Cl_2]$ and $[PtX_3(CO)]^-$ are quite stable.

$[Ni(CO)_4]$ is readily oxidized by air and can be reduced by alkali metals in liquid ammonia or thf to yield a series of polynuclear carbonylate anion
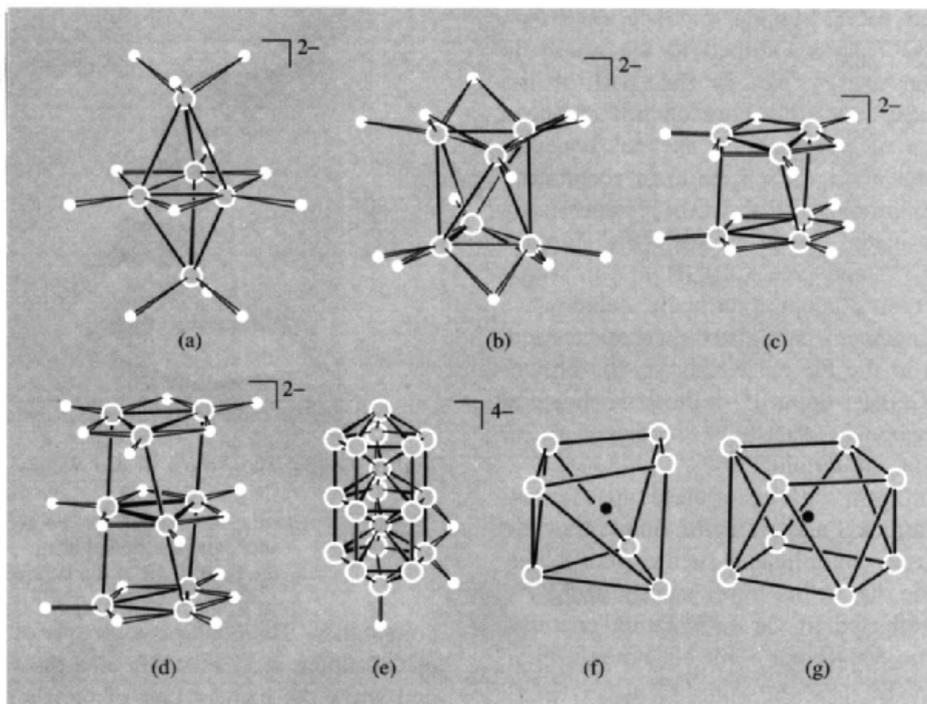
Figure 27.12 Some carbonylate anion clusters of nickel and platinum: (a) $[Ni_5(CO)_{12}]^{2-}$, (b) $[Ni_6(CO)_{12}]^{2-}$, (c) $[Pt_6(CO)_{12}]^{2-}$, (d) $[Pt_9(CO)_{18}]^{2-}$, (e) the Pt_{19} core of $[Pt_{19}(CO)_{22}]^{4-}$ showing one of the 10 bridging COs and 2 of the 12 terminal COs (which are attached to each of the 6 metal atoms at each end of the ion), (f) the Ni_7C core of $[Ni_7(CO)_{12}C]^{2-}$, (g) the Ni_8C core of $[Ni_8(CO)_{16}C]^{2-}$. Clusters (c) and (d) are structural motifs found in Ni clusters of nuclearities up to 34 and 38[35].

clusters but consisting mainly of $[Ni_5(CO_{12})]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$. The latter, being more stable and less toxic than the monomer, is a common starting material for the preparation of other clusters,[34] many of which are stabilized by encapsulated atoms of which carbon is especially efficacious. These clusters, which in general are intensely coloured and air-sensitive, have structures[35] based on the stacking of Ni_3 triangles and Ni_4 squares and, in carbon-centred clusters of higher nuclearities, based on Ni_7C and Ni_8C moieties (Fig. 27.12). Other clusters, derived from reactions of $[Ni_6(CO)_{12}]^{2-}$ and main group

reactants, have icosahedral frameworks[36] such as $Ni_{10}Se_2$, Ni_9Te_3 and $Ni_{10}Sb$. Some of these are centred with Ni, some centred with the main group element and others uncentred.

Reductions of $[PtCl_6]^{2-}$ in an atmosphere of CO provide a series of clusters, $[Pt_3(CO)_6]_n{}^{2-}$ ($n = 1-6, 10$) consisting of stacks of Pt_3 triangles in slightly twisted columns; $Pt-Pt = 266$ pm in triangles, $303-309$ pm between triangular planes (Fig. 27.12). A feature of these and other Pt clusters is that they mostly have electron counts lower than predicted by the usual electron counting rules. In the series just mentioned for instance, $n = 1$ and $n = 2$ have electron counts of 44 and 86 whereas 48 and 90 would

[34] J. K. BEATTIE, A. F. MASTERS and J. T. MEYER, *Polyhedron*, **14**, 829–68 (1995).

[35] A. F. MASTERS and J. T. MEYER, *Polyhedron* **14**, 339–65 (1995).

[36] A. J. KAHAIAN, J. B. THODEN and L. F. DAHL *J. Chem. Soc., Chem. Commun.*, 353–5 (1992).

be expected for a triangle and trigonal prism respectively. This is ascribed to the relatively large 6s–6p energy gap in this part of the periodic table and the consequently reduced involvement of p-orbitals in skeletal bonding. Heating salts of the $n = 3$ anion in acetonitrile under reflux produces $[Pt_{19}(CO)_{22}]^{4-}$ containing two encapsulated metal atoms (Fig. 27.12e). $[Pt_{26}(CO)_{32}]^{3-}$ and $[Pt_{38}(CO)_{44}H_x]^{2-}$, in which the metal atoms adopt a virtually cubic close packed arrangement, have also been characterized. In contrast to the Pt_6 cluster above, the brown-black $[Pt_6(CO)_6(\mu\text{-dppm})]^{2+}$ is the first octahedral platinum carbonyl cluster to be characterized. All its CO groups are terminal.[36a]

Palladium forms clusters of these types far less readily than nickel and platinum, unless they are stabilized by σ-donor ligands such as phosphines. This may be due to the lower energy of Pd–Pd bonds as reflected in the sublimation energies, 427, 354 and 565 kJ mol^{-1} for Ni, Pd and Pt.

Cyclopentadienyls

Nickelocene, $[Ni^{II}(\eta^5\text{-}C_5H_5)_2]$, is a bright green, reactive solid, conveniently prepared by adding a solution of $NiCl_2$ in dimethylsulfoxide to a solution of KC_5H_5 in 1,2-dimethoxyethane. It has the sandwich structure of ferrocene, and is similarly susceptible to ring-addition reactions, but its 2 extra electrons ($\mu_e = 2.86$ BM) must be accommodated in an antibonding orbital (p. 938). The orange-yellow, $[Ni(\eta^5\text{-}C_5H_5)_2]^+$, cation is therefore easily obtained by oxidation and the "triple-decker sandwich" cation, $[Ni_2(\eta^5\text{-}C_5H_5)_3]^+$ (Fig. 27.13), is produced by reacting nickelocene with a Lewis acid such as BF_3. This latter cation is a 34 valence electron species [i.e. $(2 \times 8) + (3 \times 6)$ for $2Ni^{II}$ and $3C_5H_5{}^-$] and there are theoretical grounds for supposing that this, and the 30-electron configuration, will offer the same sort of stability for binuclear sandwich compounds that the 18-electron configuration offers for mononuclear
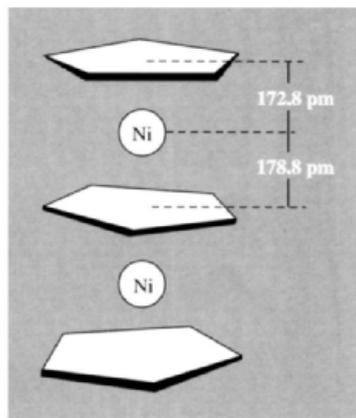
Figure 27.13 The "triple-decker sandwich" cation, $[Ni_2(\eta^5\text{-}C_5H_5)_3]^+$. Note that the C_5H_5 rings are neither "staggered" nor "eclipsed", and the nickel atoms are closer to the outer than to the central ring.

compounds. The cyclopentadienyls of palladium and platinum are less stable than those of nickel, and while the heavier pair of metals form some monocyclopentadienyl complexes, neither forms a metallocene.

## Alkene and alkyne complexes[37]

These are important not only for their part in stimulating the development of bonding theory (for a fuller discussion, see p. 931) but also for their catalytic role in some important industrial processes.

Apart from some Pd^0 and Pt^0 biphosphine complexes, the alkene and alkyne complexes involve the metals in the formally divalent state. Those of Ni^{II} are few in number compared to those of Pd^{II}, but it is Pt^{II} which provides the most numerous and stable compounds of this type. These are of the forms $[PtCl_3Alk]^-$, $[PtCl_2Alk]_2$ and $[PtCl_2Alk_2]$. They are generally prepared by treating an M^{II} salt with the hydrocarbon when a less strongly bonded anion is displaced. Thus, Zeise's salt (p. 930) may be obtained by prolonged shaking of a solution of K_2PtCl_4 in

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[36a] L. HAO, G. J. SPIVAK, J. XIAO, J. J. VITTAL and R. J. PUDDEPHATT *J. Am. Chem. Soc.* **117**, 7011–12 (1995).

[37] V. G. ALBANO, G. NATILE and A. PANUNZI, *Coord. Chem. Revs.* **133**, 67–114 (1994).

dil HCl with C_2H_4, though the reaction can be speeded-up by the addition of a small amount of $SnCl_2$. Treatment of an ethanolic solution of the product with conc HCl then affords the orange dimer, $[\{PtCl_2(C_2H_4)\}_2]$. If this is then dissolved in acetone at $-70°C$ and further treated with C_2H_4, yellow, unstable crystals of the *trans*-bis(ethene) are formed:
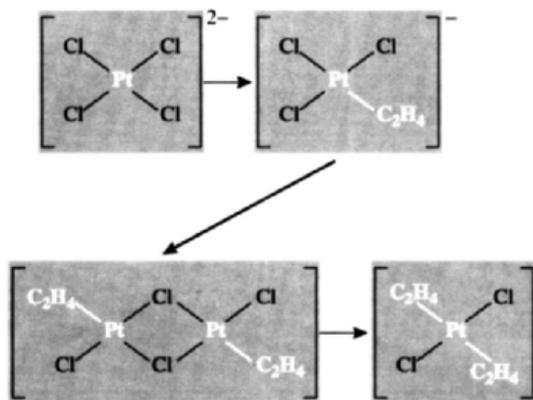

cis-Substituted dichloro complexes are obtained if chelating dialkenes such as *cis-cis*-cycloocta-1,5-diene (cod) are used (p. 932).

A common property of coordinated alkenes is their susceptibility to attack by nucleophiles such as OH^-, OMe^-, $MeCO_2^-$, and Cl^-, and it has long been known that Zeise's salt is slowly attacked by non-acidic water to give MeCHO and Pt metal, while corresponding Pd complexes are even more reactive.[38] This forms the basis of the Wacker process (developed by J. Smidt and his colleagues at Wacker Chemie, 1959–60) for converting ethene (ethylene) into ethanal (acetaldehyde) — see Panel overleaf.

Alkyne complexes are essentially similar to the alkenes (p. 932) and those of Pt^{II}, particularly when the alkyne incorporates the *t*-butyl group, are the most stable. Ni^{II} alkyne complexes are less numerous and generally less stable but are of greater practical importance because of their role as intermediates in the cyclic oligomerization of alkynes, discovered by W. Reppe (see Panel).

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[38] A. HEUMANN, K.-J. JENS and M. REGLIER, *Prog. Inorg. Chem.* **42**, 483–576 (1994).

π-Allylic complexes

The preparation and bonding of complexes of the η^3-allyl group, $CH_2{=}CH{-}CH_2{-}$, have already been discussed (p. 933). This group, and substituted derivatives of it, may act as σ-bonded ligands, but it is as 3-electron π-donor ligands that they are most important. Crudely:
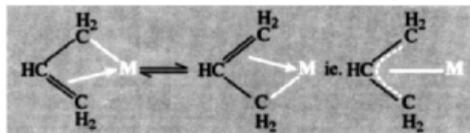
The π-allyl complexes of Pd^{II}, e.g. $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X = Cl, Br, I), are very stable and more numerous than for any other metal, and neither Ni nor Pt form as many of these complexes. Indeed, the contrast between Pd and Pt is such that in reactions with alkenes, where a particular compound of Pt is likely to form an alkene complex, the corresponding compound of Pd is more likely to form a π-allyl complex. The role of the Pd and Ni complexes as intermediates in the oligomerization of conjugated dienes (of which 1,3-butadiene, C_4H_6, is the most familiar) have been extensively studied, particularly by G. Wilke and his group. For instance in the presence of $[Ni(\eta^3\text{-}C_3H_5)_2]$ (or $[Ni(acac)_2]_3 + Al_2Et_6$), butadiene trimerizes, probably via the catalytic cycle:

*trans, trans, trans*-cyclo-dodeca-1,5,9-triene (cdt)
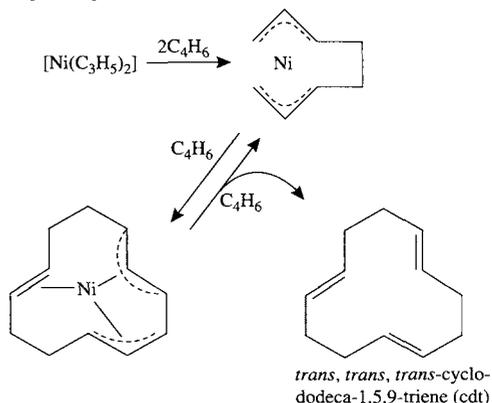
Other isomers of cdt are also obtained and, if a coordination site on the nickel is blocked by the addition of a ligand such as a tertiary phosphine, dimerization of the butadiene, rather than trimerization, occurs.

Catalytic Applications of Alkene and Alkyne Complexes

The Wacker process

Ethanal is produced by the aerial oxidation of ethene in the presence of $PdCl_2/CuCl_2$ in aqueous solution. The main reaction is the oxidative hydrolysis of ethene:

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow MeCHO + Pd\downarrow + 2HCl$$
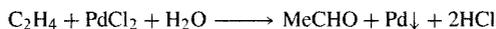
The mechanism of this reaction is not straightforward but the crucial step appears to be nucleophilic attack by water or OH^- on the coordinated ethene to give σ-bonded $-CH_2CH_2OH$ which then rearranges and is eventually eliminated as MeCHO with loss of a proton.

The commercial viability of the reaction depends on the formation of a catalytic cycle by reoxidizing the palladium metal *in situ*. This is achieved by the introduction of $CuCl_2$:

$$Pd + CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

Because the solution is slightly acidic, the $CuCl_2$ itself can be regenerated by passing in oxygen:

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O$$
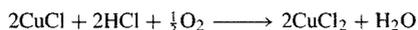
The overall reaction is thus:

$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow MeCHO$$

The Reppe Synthesis

Polymerization of alkynes by Ni^{II} complexes produces a variety of products which depend on conditions and especially on the particular nickel complex used. If, for instance, *O*-donor ligands such as acetylacetone or salicaldehyde are employed in a solvent such as tetrahydrofuran or dioxan, 4 coordination sites are available and cyclotetramerization occurs to give mainly cyclo-octatetraene (cot). If a less-labile ligand such as PPh_3 is incorporated, the coordination sites required for tetramerization are not available and cyclic trimerization to benzene predominates (Fig. A). These syntheses are amenable to extensive variation and adaptation. Substituted ring systems can be obtained from the appropriately substituted alkynes while linear polymers can also be produced.
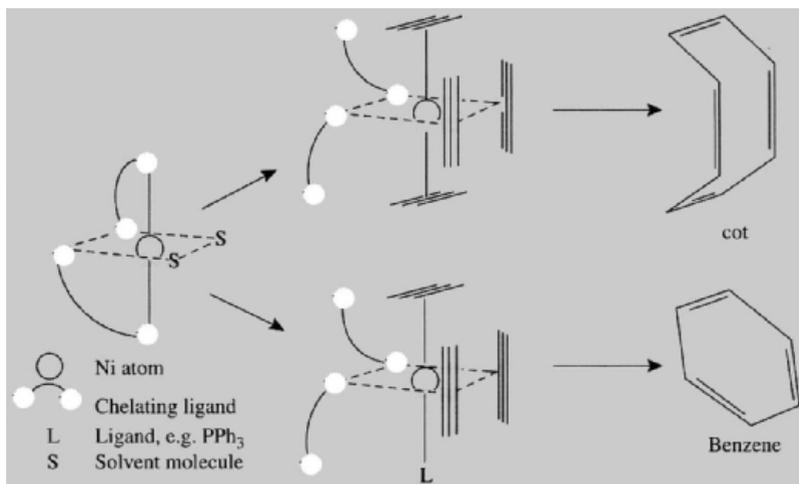
Figure A Cyclic oligomerizations of acetylene: tetramerization producing cyclooctatetraene (cot) and trimerization producing benzene.