# Synthesis and Properties of $\mu$-Ethynediyl-bis[*trans*-chlorobis(trimethylphosphine)-metal] Complexes

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The title complexes of platinum and palladium have been prepared; they provide the first examples of $\mu$-ethynediyl complexes of group 8 metals.

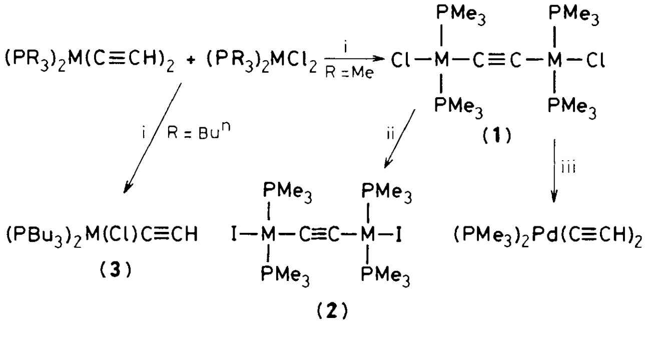
There are many possible bonding modes of acetylene ligands in organometallic compounds.[1] Bonding in an $\eta^2$ $(\sigma,\sigma)$ fashion is one of the principal modes, but has not previously been found for group 8 metal compounds,[2] although it is common for elements of groups 1, 2, and 4.

Recently we reported a convenient synthesis of transition metal acetylide complexes by the direct reaction of a terminal alkyne with a metal halide in the presence of a copper(I) halide catalyst.[3] Here we report alternative syntheses (Scheme 1), as well as the properties, of the $\mu$-ethynediyl-palladium (**1a**) and -platinum (**1b**); these are the first examples of $\mu$-ethynediyl complexes of group 8 metals.

*trans*-Di(ethynyl)bis(trimethylphosphine)palladium was treated with dichlorobis(trimethylphosphine)palladium (molar ratio 1/3) in the presence of copper(I) chloride as catalyst in diethylamine at room temperature under a dinitrogen atmosphere. After 3 h the white solid was separated off and purified by chromatography on alumina with dichloromethane as eluant. Recrystallisation from dichloromethane–hexane gave pale yellow crystals of complex (**1a**) in 53% yield, decomp. 181—184 °C. An analogous reaction gave the platinum complex (**1b**) in 61% yield, colourless crystals from methanol, decomp. 230—234 °C.

The new $\mu$-ethynediyl complexes were characterised by spectral analyses and gel permeation chromatography. The field-desorption mass spectra showed molecular ions: $m/z$ 610 for (**1a**) and 788 for (**1b**). No i.r. $\nu_{C\equiv C}$ absorption was observed for (**1a**) or (**1b**); such modes would be symmetry-forbidden. The $^{13}C\{^1H\}$ n.m.r. spectrum of (**1a**) showed the acetylenic carbon resonance at $\delta$ 101.91, and the PMe$_3$ ligand resonance at $\delta$ 15.15 (virtual t, $J_{C-P}$ 15.6 Hz). The $^{31}P$ resonance of (**1a**) appeared at $\delta$ 9.76 p.p.m. (s, high field from PPh$_3$ as reference), indicating the *trans*-configuration. These spectral data are consistent with the proposed structure (**1**).

A similar reaction of di(ethynyl)bis(tri-n-butylphosphine)-palladium with dichlorobis(tri-n-butylphosphine)palladium



**Scheme 1.** *Reagents:* i, CuCl catalyst, HNEt$_2$; ii, KI, CH$_2$Cl$_2$; iii, HC≡CH, CuCl catalyst, HNEt$_2$.

did not give the μ-ethynediyl complex, but instead yielded *trans*-chloroethynylbis(tri-n-butylphosphine)palladium (**3**), possibly owing to steric factors due to the bulky tributylphosphine ligands.

Complexes (**1a**) and (**1b**) are soluble in dichloromethane, but sparingly soluble in aromatic hydrocarbons or ethers. The terminal chloride ligands in (**1**) are easily replaced by iodide by treatment with an excess of KI in dichloromethane. In an attempt to introduce an ethynyl group as a terminal ligand, complex (**1a**) was treated with gaseous acetylene in the presence of CuI in diethylamine; however cleavage of the M–C≡C–M bridge was observed, with formation of di(ethynyl)bis(trimethylphosphine)palladium. The relatively weak M–C≡C bond in the μ-ethynediyl complex may be interpreted mainly in terms of the strong electron-donating properties of the bis(trialkylphosphine)palladium moiety[4] which causes a decrease in acidity of the ethynediyl group.

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## References

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