Metallacarbynes mimicking Alkynes in their Reactions with Palladium–Carbon Bonds

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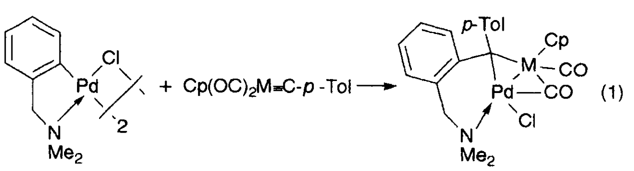
Reaction of Group 6 metallacarbynes with cyclopalladated dimers leads to C–C bond formation, for which reaction an intermediate has been characterized by X-ray diffraction methods; both structural data and extended Hückel calculations suggest the metallacarbyne to be η^1-bonded to Pd *via* the carbyne carbon atom.

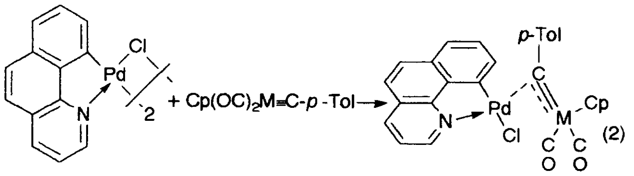
The isolbal analogy between Group 6 metallacarbynes and alkynes has been used extensively for the synthesis of polymetallic compounds, by adding $L(OC)_2M{\equiv}CR$ (L = 5e ligand) to coordinatively unsaturated metal complexes.[1] Very few studies though report the use of this concept for obtaining actual C–C bond formation.[2,3] We have found that treating the cyclopalladated dimer **1** with 2 equivalents of $Cp(OC)_2M{\equiv}C{-}C_6H_4{\cdot}p\text{Me}$ (M = Mo, W) at room temp. in dichloromethane for 1–3 h affords the bimetallic species **2** in more than 65% yield (eqn. 1). The structures of **2a** and **b** are based upon their



(1)

1

2a; M = Mo
2b; M = W



(2)

3

4a; M = Mo
4b; M = W

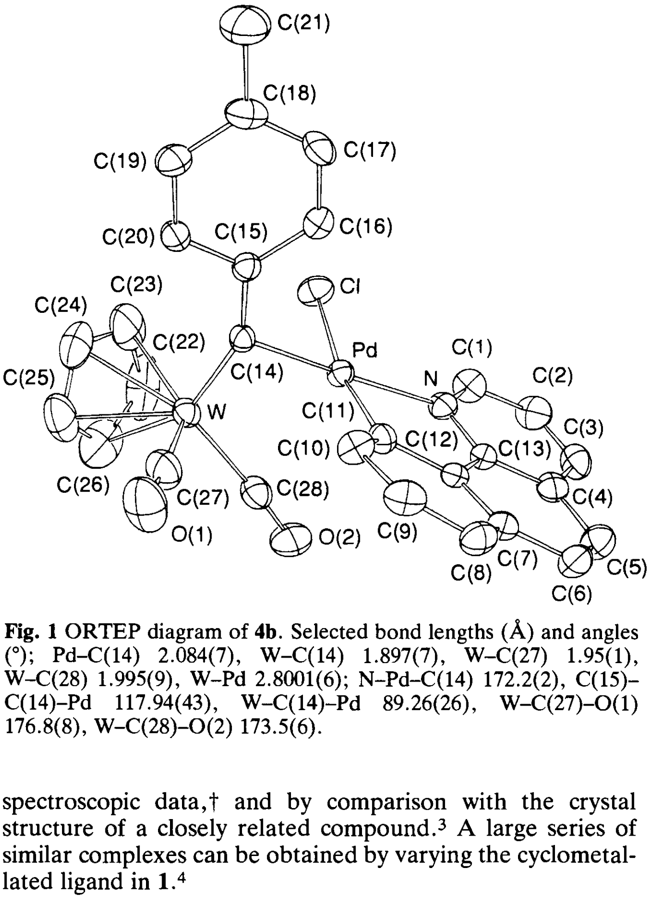
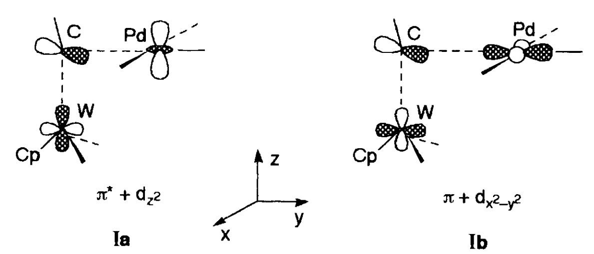


Fig. 1 ORTEP diagram of **4b**. Selected bond lengths (Å) and angles (°); Pd–C(14) 2.084(7), W–C(14) 1.897(7), W–C(27) 1.95(1), W–C(28) 1.995(9), W–Pd 2.8001(6); N–Pd–C(14) 172.2(2), C(15)–C(14)–Pd 117.94(43), W–C(14)–Pd 89.26(26), W–C(27)–O(1) 176.8(8), W–C(28)–O(2) 173.5(6).

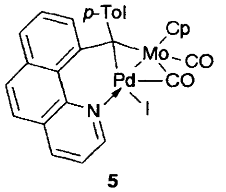
spectroscopic data,† and by comparison with the crystal structure of a closely related compound.[3] A large series of similar complexes can be obtained by varying the cyclometallated ligand in **1**.[4]

Our previous studies on the reaction of alkynes with compounds of type **1** have shown that the nature of the cyclometallated ligand determines whether the insertion of



Ia

Ib



5

alkynes occurs.[5] Among the complexes with a less reactive Pd–C bond is compound **3**, which reacts with $Cp(OC)_2M{\equiv}C\text{-}C_6H_4\text{-}p\text{Me}$ (M = Mo, W) to give a novel type of product **4** in about 65% yield (eqn. 2).

The spectroscopic data for **4** are quite different from those of **2a** and **b**.† Particularly diagnostic of a different bonding mode in **4** are the values of ν_{CO}, which are close to those of the free metallacarbynes. Moreover, neutral ligands such as pyridine react with **4** to give a monomeric compound similar to **4**, in which the metallacarbyne has been replaced by the ligand. The structure of **4b** has been established by a single crystal X-ray diffraction study (Fig. 1).‡

It is at first sight apparent that no C–C bond has been formed between the carbyne carbon atom C(14) and the carbon atom C(11) of the benzo(*h*)quinoline ligand. The Pd^{II} atom is in a normal square planar geometry while the W–C(14) bond is coordinated perpendicularly to this plane. The W–C(14) distance is intermediate between the triple bond in the free metallacarbyne[6] and that found in a complex in which the metallacarbyne is η^2-bonded to a Pt^0 fragment.[7] An important dihedral angle (57.07°) exists between the planes W–C(14)–Pd and Cp′–W–C(14) (Cp′ is the centroid of the Cp ligand), which is not observed for complexes with an η^2-bonded metallacarbyne.[8]

Extended Hückel calculations carried out on $[Cp(OC)_2W{\equiv}C\text{-}Me][Pd(Me)Cl(N_3H)]$ with a geometry taken from **4b** show that the stability of **4b** is due to two stabilizing charge transfer interactions. Interaction **Ia** occurs between the empty π^* orbital of the metallacarbyne fragment and the doubly occupied d_{z^2} orbital of Pd. Interaction **Ib** is between the doubly occupied π orbital of the metallacarbyne and the empty $d_{x^2-y^2}$ orbital of Pd. Overlap arguments indicate that the electron donation from the metallacarbyne to the Pd centre **Ib** is stronger than the reverse **Ia**. Thus, the palladium centre may be considered as a Lewis acid. The theoretical data do not support the existence of a direct Pd–W bond in **4b**. This

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† *Selected spectroscopic data* (^{1}H NMR at 200 MHz in $CDCl_3$, δ in ppm to Me_4Si, J in Hz; IR in CH_2Cl_2, ν/cm^{-1}) for **2a**: ^{1}H NMR, 2.33 s, 3 H, *p*-Me), 2.42 (s, 3 H, NMe), 2.53 (s, 3 H, NMe), 2.96 and 3.25 (AB, 2H, $^2J_{H,H}$ 11, CH_2), 4.63 (s, 5 H, η^5-C_5H_5), 6.74 (d, 1 H, $^3J_{H,H}$ 8, Ar-H); IR ν_{CO}: 1975s, 1829m. For **2b**: ^{1}H NMR, 2.32 (s, 3 H, *p*-Me), 2.38 (s, 3 H, NMe), 2.52 (s, 3 H, NMe), 3.11 and 3.29 (AB, 2 H, $^2J_{H,H}$ 12, CH_2), 4.71 (s, 5 H, η^5-C_5H_5), 6.73 (d, 1 H, $^3J_{H,H}$, 9, ArH); IR ν_{CO}: 1964s, 1827m. For **4a**: ^{1}H NMR, 2.33 (s, 3 H, *p*-Me), 5.76 (s, 5 H, η^5-C_5H_5), 9.71 (d, 1 H, $^3J_{H,H}$ 5, ArH); IR ν_{CO}: 1998s, 1932m. For **4b**: ^{1}H NMR, 2.29 (s, 3 H, *p*-Me), 5.91 (s, 5 H, η^5-C_5H_5), 9.72 (dd, 1H, $^3J_{H,H}$ 5, Ar-H; IR ν_{CO}: 1984s, 1913m. For **5**: ^{1}H NMR, 2.23 (s, 3 H, *p*-Me), 4.73 (s, 5 H, η^5-C_5H_5), 6.49 (d, 1 H, $^3J_{H,H}$ 8, Ar-H), 6.86 (d, 1 H, $^3J_{H,H}$ 8, Ar-H), 9.45 (d, 1 H, $^4J_{H,H}$ 4, Ar-H); IR ν_{CO}: 1974s, 1824m.

‡ *Crystal data* for **4b**: $C_{28}H_{20}NO_2Cl$ PdW, M_r = 728.18, orthorhombic, *Pbca*, a = 16.892(4), b = 17.028(3), c = 17.236(4) Å, V = 4958 Å^3, Z = 8, D_c = 1.951 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å (graphite monochromated), T = 293 K. An Enraf-Nonius CAD4-F diffractometer was used to collect 4851 reflections ($2 < \theta < 25°$) on a crystal of dimensions 0.21 × 0.32 × 0.38 mm. Of these, 2667 were observed [$I > 3\sigma(I)$]. All non-hydrogen atoms were located by the heavy atom method and refined anisotropically. The hydrogen atoms were included as idealized contributions. R = 0.025, R_w = 0.033, goodness of fit = 1.00, final residual = 0.18 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

is only precedented by the complex $MeCp(CO)_2Mn{=}C[Co(CO)_4]C_6H_5$, for which however, no crystal structure is available.[9] The latter example should involve a $Co(CO)_4$ unit acting as a Lewis base towards the electrophilic carbyne carbon atom.

The metallacarbyne ligand in **4b** is an isolabal analogue of an alkyne η^1-bonded to a metal centre. The latter has been proposed as an intermediate structure in the η^2-alkyne–vinylidene rearrangement occurring in d^6 ML_5 and T-shaped d^8 ML_3 alkyne complexes,[10] in our case the η^1 metallacarbyne structure is more stable than a hypothetical η^2-structure.§

We can show that the η^1-bonding mode of the metallacarbyne to the Pd fragment in **4b** is that of a true intermediate in the formation of compounds of type **2**. Indeed, reaction of **3** (where chloride has been exchanged for iodide) with $Cp(OC)_2Mo{\equiv}CC_6H_4{\cdot}p\text{Me}$ at room temp. in dichloromethane leads first to a compound analogous to **4a**, which then evolves within 2 h to give another compound **5**, whose spectroscopic data suggest a structure analogous to **2**.†

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§ In the present calculations, the geometry of the η^2-complex was derived according to ref. 8 from the η^1-complex, by reducing the angle C(14)–Pd–N from 180 to 149.1°, with the Pd–N bond pointing between the W and C(14) atoms. All other geometrical parameters were kept constant.