

## Selective Double Insertion of Isocyanides into the Metal–Carbon Bond of $\mu$ -Ethyne-dipalladium Complexes

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$\mu$ -Ethyne-diy-bis[*trans*-chlorobis(trialkylphosphine)palladium] complexes undergo the selective double insertion of aryl isocyanides into just one of the two M–C bonds.

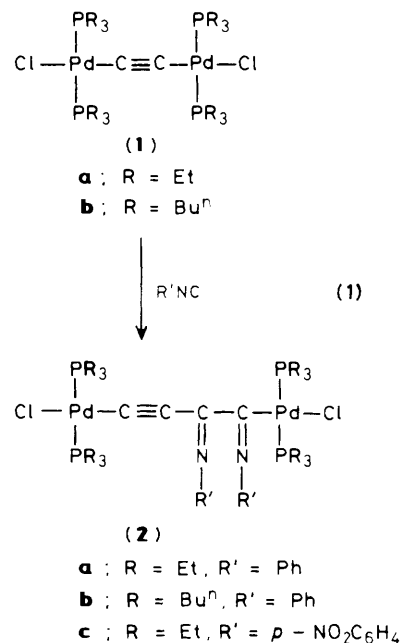
We have recently reported the synthesis of  $\mu$ -ethyne-dipalladium and -diplatinum complexes, the first examples of such complexes for group 10 metals.<sup>1</sup> The  $\mu$ -ethyne-diy dinuclear complexes are expected to have novel properties since they possess a pair of M–C  $\sigma$ -bonds which influence each other through the carbon–carbon triple bond. We have examined the reactivity of the palladium complexes and found that they undergo a novel double insertion of isocyanides selectively into one of the two M–C  $\sigma$ -bonds in the  $\mu$ -ethyne-diy-dipalladium complexes.

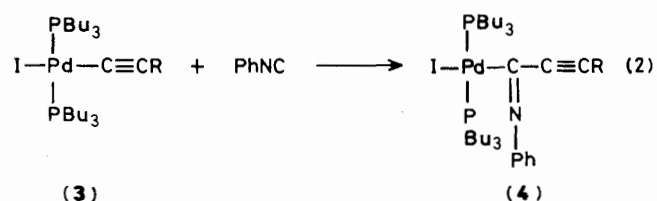
Thus, complex (**1a**)<sup>1</sup> was treated with phenyl isocyanide (2 equiv.) in benzene under nitrogen. The reaction proceeded smoothly at room temperature. After 8 h the yellow product was purified by chromatography on alumina, with benzene–dichloromethane (1 : 1) as eluant, and then recrystallized from toluene–hexane to give air-stable orange crystals of (**2a**) in 69% yield [reaction (1)], which showed double melting behaviour at 88–89 and 118–119 °C.

Complex (**2a**) was characterized spectroscopically. The field desorption mass spectrum (f.d.m.s.) exhibited the molecular ion ( $m/z$  986) corresponding to the product derived from one molecule of (**1a**) and two molecules of PhNC. The i.r. spectrum showed a strong absorption at 2090  $\text{cm}^{-1}$  due to  $\nu(\text{C}\equiv\text{C})$ , and the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. signals appeared as two singlets at  $\delta$  18.59 and 24.92 p.p.m. ( $\text{PPh}_3$  reference) in a 1 : 1 ratio, indicating that only one of the two M–C bonds in (**1a**) had undergone insertion of PhNC. These data suggest the structure (**2a**) in which double insertion of PhNC occurs just at one M–C bond of (**1a**) with the other remaining intact. The proposed structure was consistent with  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra with two sets of signals due to the phenyl, imino, and ethyl groups, *i.e.*, indicating an unsymmetrical structure of (**2a**). This structure is supported by preliminary X-ray structural analysis.<sup>2</sup> Similarly the reactions of (**1a**) with

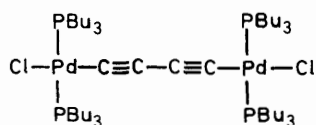
*p*-nitrophenyl isocyanide and of (**1b**) with phenyl isocyanide gave the double insertion products (**2b**) and (**2c**), respectively, in good yields.

However, reactions of palladium–acetylide complexes such as (**3a**) and (**3b**), and the  $\mu$ -butadienyne-dipalladium complex (**5**) with phenyl isocyanide gave exclusively normal single insertion products (**4**) and (**6**), respectively [reactions (2) and (3)]. These results indicate that the double insertion of RNC is characteristic of the  $\mu$ -ethyne-diy-dipalladium complexes.





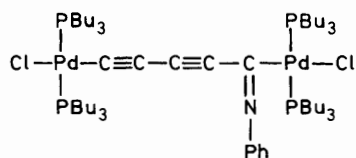
(3)

**a** ; R = H**b** ; R = Ph

(5)

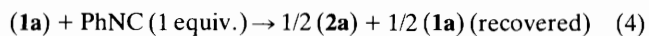


(3)



(6)

It should be noted that the reaction between (**1a**) and PhNC (1 equiv.) gave no single insertion product analogous to (**6**), but instead yielded (**2a**), with recovery of about half of the starting material (**1a**) [reaction (4)]. Moreover no further reaction of (**2a**) with PhNC was observed. This suggests that the double insertion occurs selectively, regardless of the molar ratio of RNC to the complex, although the reaction mechanism is not understood at present. Although it is well established<sup>3</sup> that isocyanides insert into the M-C bond of some transition metal complexes in several ways, our result may provide the first examples of the selective double insertion of RNC.



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### References

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