E2-44 Cyclisation of $MeO_2CC{\equiv}CCO_2Me$ at a rhodium centre forming a (P-N-O-C) ligand

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Dimethlyl acetylenedicarboxylate (DMA) often forms adducts with metals which are in a low valency state. Sometimes such an interaction is followed by carbon-carbon bond formation giving etallacyclopentadienes or hexacarbomethoxybenzene, for example, treatment of *trans* $[RhCl(CO)(PPh_3)_2]$ with DMA gives hexacarbomethoxybenzene. In this communication, the formation of a (P-N-O-C) ligand by the reaction of DMA with a Rh(I) complex containing an anionic (P-N-O) ligand $PPh_2CH_2C(Bu^t)$=N-N=C(Ph)O^- is presented - treatment of *Z*-$PPh_2CH_2C(Bu^t)$=$NNMe_2$, with benzoyl hydrazide ($PhCONHNH_2$) gave the phosphino-N-benzoylhydrazone *Z*-$PPh_2CH_2C(Bu^t)$=NNHC(=O)Ph (**1**). The Rh(I) complex (**2**) was made by the reaction of (**1**) with 0.5 equivalent of $[Rh_2Cl_2(CO)_4]$.
Teatment of (**2**) in dichloromethane with an excess of DMA gave the cyclometallated complex (**3**) as a single product.

The X-ray crystal structure of (**3**) showed that (I) one acetylenic carbon of DMA had attacked the CH_2 carbon of the terdentate (P-N-O) ligand in (**2**) and the other acetylenic carbon was bonded to rhodium to give a tetradentate (P-N-O-C) ligand with 3 fused 5-membered rings, (ii) the second DMA had become bonded to rhodium as an olefinic ligand. When (**3**) was heated in benzene it isomerised to the complex (**4**); in this isomer the terminal olefinic ligand is *trans* to P whereas in (**3**) it is *cis* to P.