

E2-44 Cyclisation of MeO₂CC=CCO₂Me at a rhodium centre forming a (P-N-O-C) ligand

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Dimethyl 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 metallacyclopentadienes or hexacarbomethoxybenzene, for example, treatment of *trans* [RhCl(CO)(PPh₃)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 PPh₂CH₂C(Bu')=N-N=C(Ph)O⁻ is presented. Treatment of *Z*-PPh₂CH₂C(Bu')=NNMe₂, with benzoyl hydrazide (PhCONHNH₂) gave the phosphino-N-benzoylhydrazone *Z*-PPh₂CH₂C(Bu')=NNHC(=O)Ph (1). The Rh(I) complex (2) was made by the reaction of (1) with 0.5 equivalent of [Rh₂Cl₂(CO)₄]. Treatment 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 CH₂ 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.