E2-43 Rhodium complexes of a novel (P-N-O) ligand $PPh_2CH_2C(Bu^t)=NNHC(=O)Ph$

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Tertiary phosphine complexes of rhodium are being widely used as catalysts for may organic transformations, for example, the Wilkinson's catalyst $[RhCl(PPh_3)_3]$. Therefore it is or interest to prepare new phosphine ligands and to investigate their coordination and organometallic chemistry. Treatment of $Z\text{-}PPh_2CH_2C(Bu^t)=NNMe_2$ with benzoyl hydrazide ($PhCONHNH_2$) gave the phosphino-N-benzoylhydrazone $Z\text{-}PPh_2CH_2C(Bu^t)=NNHC(=O)Ph$ (1). One would expect the mono-deprotonated form of (1), $PPh_2CH_2C(Bu^t)=N\text{-}N=C(Ph)O^-$, to act as an anionic terdentate ligand coordinating to a metal through P,N, and O. The synthesis of (1) and some chemistry generated from it with rhodium (I) and rhodium(III) are presented here. (1) treated with 0.5 equivalent of $[Rh_2Cl_2(CO_4)]$ in dichloromethane at 20°C caused $C\equiv O$ evolution and gave the hoped for rhodium (I) complex (2) containing 2 fused 5-membered chelate rings. The complex (2) reacted immediately with bromine to give the dibromorhodium (III) complex (3). Methyl iodide also added to (2) to give a single product which we formulate as the complex (4).

Oxidative addition of propargyl chloride ($HC\equiv CCH_2C1$) to rhodium (I) proceeded *via* the nucleophilic attack by the metal at the terminal $HC\equiv$ carbon and not the CH_2C1 carbon thus giving the allenic complex (5). In conclusion, $Z\text{-}PPh_2CH_2C(Bu^t)=NNMe_2$ was readily converted into a new phosphine ligand (1) which can act as a terdentate (P-N-O) ligand, and the reactive Rh(I) complex (2) underwent oxidative addition reactions with Br_2, MeI and propargy^1 chloride to give Rh (III) complexes.