

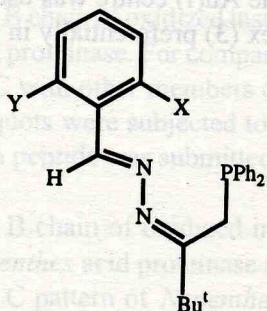
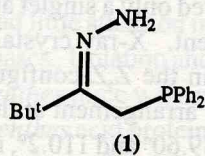
E2-22 Chelate assisted aryl halide coordination to Ru(II)

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Coordination chemistry of N-, P-, or S-donor ligands was known for >100 years but that of halocarbons (or organic halides) has a short history, since 1980s. The main reason for this is that the halogen of a halocarbon is a very poor donor. The order of donor ability of the halogen of halocarbons decreases in the following way, $RI > RBr > RCl > RF >$. The synthesis of a ligand system which, when chelated to Ru (II) through P and N, forces the halogen to coordinate to Ru(II) is presented. The azines (**2a**) - (**2d**) were prepared by condensing (**1**) with the appropriate aryl aldehyde. Treatment of (**2a**) with $[RuCl_2(PPh_3)_3]$ gave (**3a**). The phosphorus NMR spectrum of (**3a**) showed a doublet for P_B with coupling to P_A and a doublet of triplets for P_A with coupling to both fluorines and P_B . The fluorine NMR spectrum supported this observation. In the proton NMR spectrum, the CH_2 protons are equivalent and coupled only to

P_A , ${}^2J(P_A H)=14.4$ Hz and the HC=N proton is coupled to P_B , ${}^4J(P_B H)=6.8$ Hz. X-ray crystal structure determination confirmed the proposed structure and the fluorine coordination, the Ru-F bond distance is 2.366 Å. Similarly, treatment of (2b), (2c) or (2d) with $[RuCl_2(PPh_3)_3]$ gave (3b), (3c) or (3d), respectively. Their IR, 1H and ${}^{31}P$ NMR data are very similar to those of (3a), indicating that (3b), (3c) and (3d) have very similar structures.



	X	Y
a	F	F
b	Cl	H
c	Br	H
d	I	H

