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ABSTRACTS OF PAPERS

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Carbonyl Complexes of Iridium (I) with Hybrid Bidentate Ligands
Containing Phosphorus and Sulfur Donor Atoms.

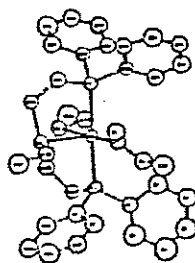
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Iridium carbonyl complexes of the type $[\text{Ir}(\text{CO})(\text{P-SR})_2]\text{BPh}_4$ have been prepared with the hybrid ligands $\text{Ph}_2\text{P-CH}_2\text{-CH}_2\text{-SR}(\text{P-SR}; \text{R} = \text{Me, Et, Ph})$. The five coordinate complexes, characterized by ir and nmr (^1H , ^{31}P) spectra, reversibly add carbon monoxide to form $[\text{Ir}(\text{CO})_2(\text{P-SR})_2]^+$ derivatives with the concomitant dissociation of a thio arm of the chelates. The five coordinate cations are stereochemically non rigid at room temperature on the nmr time scale but become stereochemically rigid at low temperature. The reactions of HBF_4 , H_2 and HCl with $[\text{Ir}(\text{CO})(\text{P-SR})_2]^+$ have also been examined and the solution structures of the isolated products have been determined using variable temperature ^{31}P nmr. The cation $[\text{Ir}(\text{CO})(\text{P-SEt})_2]^+$ reacts with methanol to give the hydridomethoxycarbonyl derivative of iridium (III) which is precipitated with sodium tetraphenyl borate as white crystalline compound $[\text{IrH}(\text{CO}_2\text{Me})(\text{P-SEt})_2]\text{BPh}_4$. The ORTEP drawing of the $[\text{IrH}(\text{CO}_2\text{Me})(\text{P-SEt})_2]^+$ cation is shown in figure.



The coordination around the iridium atom can be described in terms of a slightly distorted octahedron; four coordination positions are occupied by the P-SEt ligands and the remaining two by the hydride and the methoxycarbonyl ligand.