Synthesis and Structure of Polyoxoanion Supported Organorhodium (I) and Organoiridium (I) Complexes

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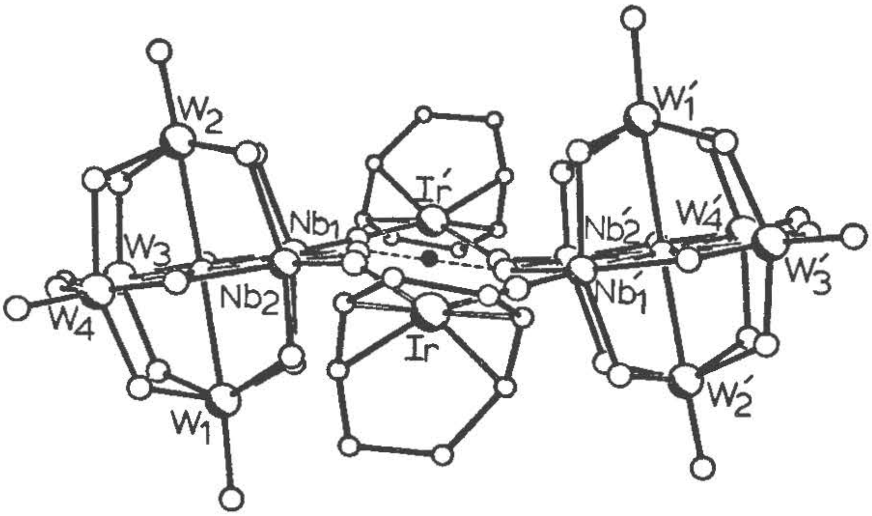
Since the first reports of polyoxoanion supported organometallic complexes in 1978-79[1a-c], numerous other supported complexes have also been reported as part of a program directed toward the synthesis and structural characterization of stable organometallic adducts.[1d-j] However, virtually nothing has been reported regarding the reactivity of this class of compounds. In an attempt to prepare more reactive polyoxoanion supported organometallic complexes and investigate their reactivity, we have decided to focus on rhodium(I) and iridium(I) polyoxoanion derivatives. In view of the extensive reaction chemistry already known for rhodium(I) and iridium(I) in solution and on oxide surfaces, it is hoped that their polyoxoanion derivatives will exhibit a broad range or reactivity and that this reactivity will contrast the well-known π-acid ligand chemistry.

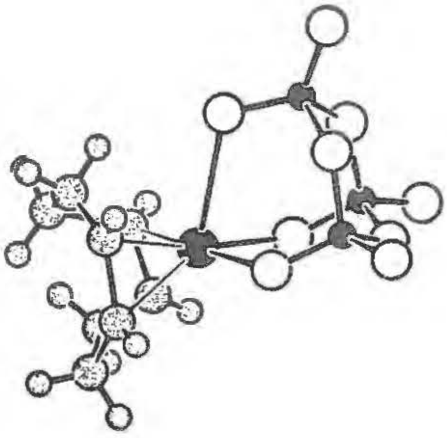
The three following $(C_8H_{12})Ir^+$ polyoxoanion adducts have been synthesized and structurally characterized: $\{[(C_8H_{12})Ir]_5(Nb_2W_4O_{19})_2\}[(\underline{n}\text{-}C_4H_9)_4N]_3$ (1), $\{[(C_8H_{12})Ir]_2H(Nb_2W_4O_{19})_2\}[(\underline{n}\text{-}C_4H_9)_4N]_5$ (3), and $\{[(C_8H_{12})Ir](P_3O_9)\}[(\underline{n}\text{-}C_4H_9)_4N]_2$ (4). NMR and IR data suggest the anion of 1 is isostructural with the anion of $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}[(\underline{n}\text{-}C_4H_9)_4N]_3$ (2) reported previously.[2] In 1, two $Nb_2W_4O_{19}^{4-}$ anions act as pentadentate bridging ligands in which both terminal and bridging oxygens are utilized to bind five $(C_8H_{12})Ir^+$ units. Single crystal X-ray diffraction studies performed by Professor Victor Day at the University of Nebraska have determined the structures of compounds 3 and 4. In the anion of 3 (see a), one two-coordinate proton and two four-coordinate $(C_8H_{12})Ir^+$ units link together the two $Nb_2W_4O_{19}^{4-}$ anions. The ONb_2 and ONb oxygens are utilized in binding to the proton and $(C_8H_{12})Ir^+$ units, respectively. In 4 the $(P_3O_9)^{3-}$ anion (see b) is bound to iridium in a tridentate fashion making the coordination geometry around Ir^I approximately square pyramidal.



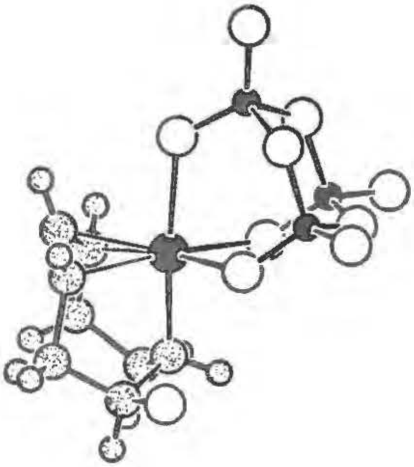
a

The metal dicarbonyl polyoxoanion adducts $\{[(CO)_2Rh]_5(Nb_2W_4O_{19})_2\}[(\underline{n}\text{-}C_4H_9)_4N]_3$ (**8**), $\{[(CO)_2Rh]_3(Nb_2W_4O_{19})_2\}[(\underline{n}\text{-}C_4H_9)_4N]_5$ (**9**), $\{[(CO)_2Ir]_2H(Nb_2W_4O_{19})_2\}[\underline{n}\text{-}C_4H_9)_4N]_5$ (**10**), and $\{[(CO)_2Ir](P_3O_9)\}[(C_6H_5)_3PNP(C_6H_5)_3]_2$ (**11**) have been prepared and characterized. Compounds **8**, **10**, and **11** are synthesized by carbonylation of their respective diene analogs, whereas compound 9 is prepared from $[Rh(CO)_2Cl]_2$ and $(Nb_2W_4O_{19})[(\underline{n}\text{-}C_4H_9)_4N]_4$. Based on IR and NMR data, compounds **8**, **10**, and **11** exhibit the same anion structures as their respective diene analogs. In the structure proposed for **9**, two $Nb_2W_4O_{19}{}^{4-}$ anions act as tridentate bridging ligands in which the terminal ONb oxygens and the bridging ONb_2 oxygen are utilized to bind three $(CO)_2Rh^+$ units. This structure is supported by ^{17}O, ^{183}W, and ^{13}C NMR data.

The novel reaction of $\{[(C_8H_{12})Ir](P_3O_9)\}[(\underline{n}\text{-}C_4H_9)_4N]_2$ (**4**) with dioxygen has been investigated. In 1,2-dichloroethane at 55-60°C, dioxygen reacts with **4** to form $\{[(\eta^1,\eta^3\text{-}C_8H_{11}OH)Ir](P_3O_9)\}[(\underline{n}\text{-}C_4H_9)_4N]_2$ (**13**). A single crystal X-ray diffraction study of 13 performed by Professor Victor Day at the University of Nebraska shows the Ir^{III} atom to be bonded to three oxygens of the $P_3O_9{}^{3-}$ ligand and to four carbons of the $C_8H_{11}OH$ ring, making the coordination geometry around iridium octahedral if the allyl function is regarded as occupying two coordination sites (see c).



b



c

References

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