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REACTIONS OF DIHYDRIDODECACARBONYLTRIOSMIUM WITH ARENE-DIAZONIUM TETRAFLUOROBORATES. SYNTHESIS AND INTERCONVERSION OF MONO- AND DIHAPTO BRIDGED ARYLAZO TRIOSMIUM CLUSTERS

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As a consequence of their relationships to transition metal-nitrosyl and transition metal-dinitrogen compounds, mononuclear transition metal arylazo compounds have been prepared and characterized in profusion during the past fifteen to twenty years[1,2]. Polynuclear transition metal compounds containing arylazo ligands, by contrast, remain relatively rare. The two structurally characterized examples have monohapto bridging arylazo ligands[3,4]; four other compounds have also been assumed to possess bridging arylazo ligands of the same structural type[5-8].

Arenediazonium salts $\text{ArN}_2^+ \text{BF}_4^-$ (Ar = p-C₆H₄CH₃, Ph, p-C₆H₄F) react with $\text{H}_2\text{Os}_3(\text{CO})_{10}$ in refluxing dichloromethane to produce the compounds $\text{HOs}_3(\text{CO})_{10}(\eta^1\text{-N=N-Ar})$ (1). The structure of $\text{HOs}_3(\text{CO})_{10}(\eta^1\text{-N=N-p-C}_6\text{H}_4\text{CH}_3)$ has been deduced by ¹⁵N NMR and confirmed by single-crystal x-ray diffraction[9].

UV ($\lambda > 297$ nm) photolyses of solutions of 1 produce the isomeric compounds $\text{HOs}_3(\text{CO})_{10}(\eta^2\text{-N=N-Ar})$ (2). The structure of $\text{HOs}_3(\text{CO})_{10}(\eta^2\text{-N=N-p-C}_6\text{H}_4\text{CH}_3)$ has been deduced by N NMR and the structure of $\text{HOs}_3(\text{CO})_{10}(\eta^2\text{-N=N-Ph})$ has been confirmed by single-crystal x-ray diffraction [10]. This compound is the first structurally characterized sample of a polynuclear transition metal compound containing a dihapto bridging arylazo ligand. Compounds 2 revert to 1 thermally.

Quantum yields for the photoisomerization of 1 to 2 have been estimated at 313 nm and 366 nm; they indicate that isomerization results primarily from the absorption of higher-energy light.

¹⁵N NMR proved useful in the determination of the solution structures of the compounds described in this work; the technique may be generally useful for other polynuclear arylazo transition metal compounds, as well.

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