Oxidation of arenetricarbonylmolybdenum(0) complexes by trithiazyl trichloride

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Oxidation of arenetricarbonylmolybdenum(0) with cyclotrithiazyl trichloride has been studied at room temperature as well as at -78°C. The effect of substituent arene group on the arene moiety has been studied.

The reactions of trithiazyl trichloride with transition metals and their compounds are an active area of research. Using these actions a large number of metal complexes have been synthesized. These reactions appear to be unusual in the sense that the nature of S-N moiety coordinated to the metal centre is sensitive to the reaction conditions and varies with slight change in any of the factors governing the reaction. Besides, the mechanistic aspects of such reactions are in an embryonic stage. In view of this and in continuation of our earlier efforts, presently we have shown the oxidation of several \( \eta^2 \)-arenetricarbonylmolybdenum(0) complexes by this reagent.

**Experimental**

All the chemicals used were of pure grade. The \( \eta^2 \)-arenetricarbonylmolybdenum(0) complexes\(^{12}\) (arene = benzene, toluene, xylene, anisole, mesitylene and hexamethylbenzene) trithiazyl trichloride\(^{13}\) (NSCl\(_3\)) and \([\text{Mo}(N_3S_2)Cl_3]\)\(^{12}\) were prepared by the literature methods. Characterization of the complexes was based on IR(KBr), magnetic measurements and X-ray powder patterns as has been reported earlier\(^{11}\).

A typical reaction was carried out as follows:

A saturated solution of (NSCl\(_3\)) in dichloromethane (10 ml) was added dropwise with stirring to a solution of benzene tricarbonylmolybdenum(0) (0.5 mmol) in dichloromethane (10 ml) at 35°C when effervescence occurred with the formation of a brown precipitate. After the gas evolution had ceased, the precipitate was filtered, washed with dichloromethane and pet. ether (40°-60°) and dried in vacuo (yield, 95%).

This procedure was followed with all the arene complexes at different temperatures (upto -78°C). In every case the same complex was isolated which was identified as \([\text{Mo}(N_3S_2)Cl_3]_2\). (Found: N, 13.2; Cl, 35.1; S, 19.9%. \([\text{Mo}(N_3S_2)Cl_3]_2\) requires N, 13.6; Cl, 34.8; S, 20.7%); IR(KBr): 950(vs)\(\nu M=N\), 340(vs)\(\nu MCI\).

The complex was further characterized by comparing its properties (analyses, spectral data, magnetic moment and X-ray powder pattern) with an authentic sample whose crystal structure has been determined by X-ray single crystal studies. Furthermore its reactions with THF, pyridine, 2,2'-bipyridyl and 2-phenanthroline yielded \([\text{Mo}(N_3S_2)Cl_3\text{THF}]_8\), \([\text{Mo}(N_3S_2)Cl_3\text{Py}]_8\), \([\text{Mo}(N_3S_2)Cl_3\text{bipy}]_14\) and \([\text{Mo}(N_3S_2)Cl_3\text{O-phen}]_14\) respectively.

**Results and discussion**

The oxidation of various ArMo(CO)\(_3\) by (NSCl\(_3\)) proceeds with immediate formation of \([\text{Mo}(N_3S_2)Cl_3]_2\) regardless of the temperature (35°C to -78°C). Analogous oxidations of arenetricarbonylmolybdenum(0) complexes using \(I_2\) and NOCl as oxidants have been reported earlier\(^{15-16}\). It seems that relatively weaker oxidising agents such as \(I_2\), lead to the formation of products having both arene and carbonyl groups bonded to the metal centre while comparatively stronger oxidising agents, such as NOCl, yield an intermediate \([\text{Mo}(CO)_2(NO)_2Cl_2]\) having no coordinated arene group but only carbonyl groups.

However, presently we observe that trithiazyl trichloride oxidation of arenetricarbonylmolybdenum(0) affords a product having neither arene nor carbonyl groups coordinated to the metal centre. All efforts to isolate an intermediate with composition \([\text{Mo}(CO)_2(NS)_2Cl_2]\) similar to \([\text{Mo}(CO)_2(NO)_2Cl_2]\) failed even at low temperature. This may be due to high reactivity and high oxidising power of (NSCl\(_3\)) (vide supra). Indirect support to the latter observation is forthcoming from the fact that NOCl reacts with \([\text{ArMo}(CO)_3]\) where \(Ar = \text{mesitylene or hexamethylbenzene, at relatively lower rates as compared to ArMo(CO)_3 where Ar = benzene or toluene}^{17}. In contrast, (NSCl\(_3\)) oxidises all the arene complexes instantaneously unlike the reaction of \(I_2\) and NOCl with arene complexes\(^{18}\). In the presently studied reactions, (NSCl\(_3\)) exhibits three functions: (i) providing \(N_3S_2\) ligand coordinated to molybdenum; (ii) oxidation of metal to +6 oxidation state; and (iii) chlorinating the metal ion.
These functions though are known in literature, but the factors that are responsible for the differences in the behaviours of (NSCI) with different metal ions or their complexes are still obscure.

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References
18 Though the reaction of \( \eta^6 \)-(hexamethylbenzene)molybdenum tricarbonyl with trithiazyl trichloride was relatively slower compared to that of other arenemolybdenum complexes, it was relatively too fast to isolate the intermediate product.