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Preliminary Communication

Use of ozone as an oxygen atom transfer agent in the synthesis of pentamethylcyclopentadienyl rhenium trioxide

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Abstract

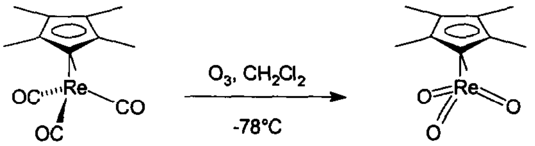
Reaction of ozone with (η-$C_5(CH_3)_5$)$Re(CO)_3$ leads to oxidative decarbonylation and a moderate to good yield of (η-$C_5(CH_3)_5$)ReO_3.

Key words: Rhenium; Oxide; Ozon; Oxidative decarbonylation

Examination of organometallic species in which the metal exists in a high formal oxidation state has become an area of intense recent interest [1], largely spurred by the development of new selective synthetic routes to metal oxo, imido, and similar complexes. Such chemistry is relevant to industrial oxidation processes [2]. One compound that has played an important role in the recent exploration of this area is Cp*ReO_3 (Cp* = η-$C_5(CH_3)_5$) [3], most thoroughly investigated by Herrmann and coworkers.

The literature on this compound reveals a number of synthetic routes, starting from the initial report (photolysis of Cp*$Re(CO)_3$ in THF in the presence of O_2) [4] and continuing through H_2O_2 oxidation of a benzene solution of tricarbonyl [5] and a recent report suggesting the use of Mn_2O_7 [6]. Investigations by Kochi and coworkers noted modest yields (40%) on use of tert-butyl hydroperoxide [7] and good to excellent yields with dimethyldioxirane [8]. The inference one takes from these is that highly reactive oxygen transfer agents are necessary to achieve high yields of the desired trioxide.

Ozone has often been used as an oxygen transfer agent in organic and inorganic chemistry [9]. Although the quintessential reaction of ozone with alkenes involves all three oxygen atoms, there are many cases of oxidation, particularly of nitrogen and sulfur, where ozone acts to transfer an electrophilic oxygen atom to a nucloephilic Lewis base [10]. Its limitations in this regard are usually overreaction and thus decomposition of product. It seemed that, given the observed stability of Cp*ReO_3 to oxidative decomposition, ozone might be a suitable oxygen transfer agent for its synthesis from the tricarbonyl (eqn. (1)).



(1)

Reaction of a stirred solution of Cp*$Re(CO)_3$ (approx. 0.01 M) in dichloromethane at −78°C with an ozone/O_2 mixture generated from a commercial ozone generator led to an initial development of the characteristic yellow color of the trioxide. No color change was observed under these conditions upon bubbling pure O_2 though the solution; only after turning on the ozone generator was any reaction noted. After approximately 15 min, a dark, tea-brown color formed, and soon thereafter, the outflow gasses caused an aqueous KI solution to darken, signalling that uptake of O_3 had ceased. Monitoring the IR spectrum of aliquots of the reaction mixture showed clean loss of the CO stretches of starting material (2008 and 1908 cm^{-1}) and growth of new Re=O peaks (905, 879 cm^{-1}); no additional metal carbonyl or oxo stretches were evident prior to eventual decomposition of product. Removal of solvent *in vacuo* followed by column chromatography led to isolation of a 50% yield of pure Cp*ReO_3.

The remainder of the reaction mixture has not been identified. Continued purging of the reaction mixture with ozone leads to gradual decomposition; examination of IR spectra suggests fragmentation and ozonolysis of the pentamethylcyclopentadiene ring as evidenced by a stretch at 1735 cm^{-1} [4b]. Therefore, care was taken to halt the reaction when rapid uptake of O_3 ceased.

While this methodology does not improve on reported yields of Cp*ReO_3 via other routes, it does have the advantage of speed and convenience. Given the current desire to examine the chemistry of M=O bonds and to find new synthetic routes to such complexes, ozone may be a particularly attractive reagent.

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It is highly reactive, yet easy to generate and quantitate. The only byproduct of the oxygen atom transfer is O_2. There are potential dangers and limitations. The desired oxo complex must be stable to oxidative cleavage of other ancillary ligands, and no reactive functionality can be present on such an ancillary ligand. It is important that, when transfer of more than one oxygen is desired, intermediates remain in solution. Care must always be exercised concerning possible generation of thermally unstable ozonides, and selection of unreactive solvents such as dichloromethane is necessary, as is true with any ozonolysis. However, it is clear that opportunities exist to extend the reactivity we observed to other systems.

Experimental details

Pentamethylcyclopentadienyl tricarbonylrhenium [11] (2.0 g, 4.94 mmol) was dissolved in 500 ml dichloromethane (freshly distilled from CaH_2). The reaction mixture was stirred at −78°C. Oxygen was passed through an OREC ozone generator operating at 0.6 amp and bubbled into the reaction mixture; the outflow was passed though an aqueous KI solution. After 30 min, the reaction mixture had turned a deep tea-colored brown, and discoloration of the KI solution indicated uptake of O_3 had ceased. Removal of solvent by rotary evaporator left a semisolid brown residue. This was flash chromatographed on silica (Baker, 230–400 mesh) using initially pure dichloromethane. Further elution of the yellow band with 0.5% ethanol in chloroform gave, on evaporation, 1.02 g (2.76 mmol, 56%) pentamethylcyclopentadienyl trioxorhenium.

Acknowledgements

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