

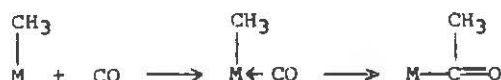
## Carbon Monoxide Activation by Actinides

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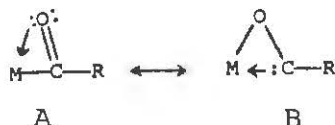
Literature Seminar

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There is currently a great academic and industrial interest in understanding processes by which carbon monoxide (ultimately derived from coal) can be converted by various metal catalysts into useful organic compounds [1]. The mechanism of homogeneous transition metal CO activation is reasonably well understood and involves the migratory insertion of CO into a metal-carbon bond producing a metal acyl [2].

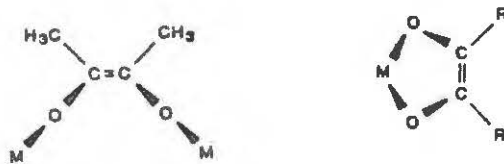


Classical acyl products of late transition metals show primarily only metal bonding to the acyl carbon. With early transition metals (Ti, Zr, Hf), however, significant bihapto acyl coordination of both the acyl carbon and oxygen is observed [3]. Nonclassical dihapto coordinated acyls have often been proposed as intermediates in the catalytic activation of CO. Intermediates such as these might be isolated by providing a metallic center with sufficient unsaturation and oxygen affinity to be stabilized by conjunctive metal-oxygen bonding.



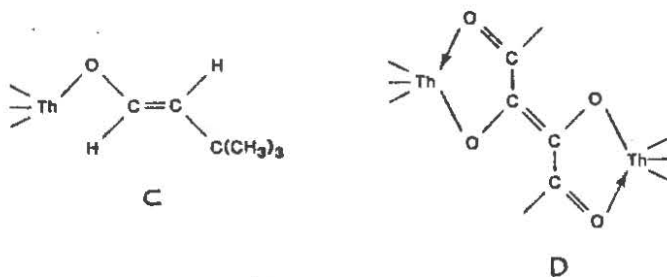
The bis(pentamethylcyclopentadienyl) actinide complexes have three unique characteristics that lend themselves to nonclassical CO activation: high coordinative unsaturation, high kinetic lability, and high oxygen affinity [4]. The bonding in organoactinide acyls involves a major contribution from a carbene-like hybrid B due to the large magnitude of the metal-oxygen interaction. As a result, actinide acyls more closely resemble early transition metal acyls and have distinctly carbene-like chemical behavior.

Actinide dimethyl complexes, as well as sterically unhindered actinide hydrides, react rapidly with CO to produce, quantitatively, both dimeric and monomeric complexes containing the cis-2-butene-2,3-diolate ligand [5].

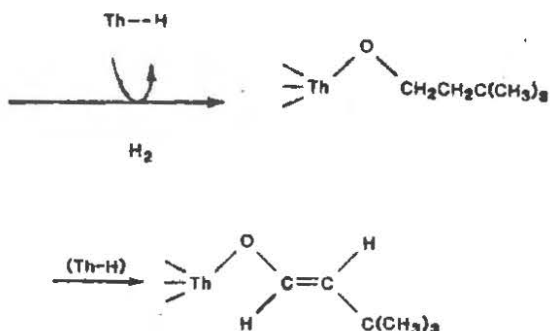


A mechanism for enediolate formation consistent with spectroscopic and kinetic data involves the insertion of the oxycarbene into an actinide hydride followed by a second CO insertion, hydrogen migration, and carbon-carbon bond formation [6].

Monomeric actinide  $\eta^2$ -acyls undergo reactions similar to the classical 1,2-hydrogen migration to produce the trans-eneolate ligand C, as well as reacting with an additional equivalent of CO to produce an enedionediolate ligand D [8].



The carbene-like reactivity of actinide  $\eta^2$ -acyls can be further exploited catalytically to produce hydrogenated products of the inserted CO [9]. Actinide acyls react with  $H_2$  in the presence of actinide hydrides to yield the corresponding alkoxide. When no  $H_2$  is present the hydrides catalyze the production of the trans-eneolate ligand.



Deuterium labeling studies detail a mechanism involving formal insertion of the carbenoid acyl carbon into a hydride bond, followed by  $\beta$ -hydrogen elimination to yield the trans-eneolate or in the presence of  $H_2$ , the alkoxide product. These reactions further underscore the oxycarbene character of organoactinide  $\eta^2$ -acyls and demonstrate that their nonclassical carbene-like reactivity can be used to produce homometallic hydrogenation and rearrangement processes.

## References

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