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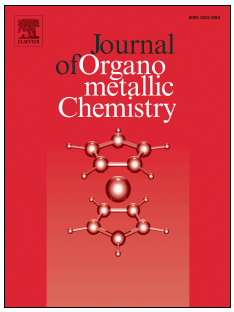

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Sterically encumbered mixed sandwich compounds of uranium(III): synthesis and reactivity with small molecules

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Dedicated to Professor W. J. Evans on the occasion of his 70th birthday. Bill, you are an inspiration to us all.

Abstract

A series of uranium(III) mixed sandwich complexes with sterically demanding Cp^R ligands, of the type $[U(COT^{TIPS2})(Cp^R)]$ (Cp^R = Cp^{tBu} ($C_5H_4{}^tBu$), Cp^{tBu2} ($C_5H_3{}^tBu_2$-1,3), Cp^{tBu3} ($C_5H_2{}^tBu_3$-1,2,4), Cp^{TIPS2} ($C_5H_3(Si^iPr_3)_2$-1,3), Cp^{Me4Bz} ($C_5Me_4CH_2Ph$), Ind^{Me6} (C_9HMe_6) and Ind^{Me7} (C_9Me_7), and COT^{TIPS2} = $C_8H_6(Si^iPr_3)_2$-1,4), have been synthesised and their X-ray crystal structures determined. The reactivity of these complexes with CO and CO_2 is reported, including the squarate complex $[U(COT^{TIPS2})(Ind^{Me6})]_2(\mu\text{-}C_4O_4)$, IR data on the long-lived carbonyl complex $[U(COT^{TIPS2})(Ind^{Me7})(CO)]$ and the carbonate complex $[U(COT^{TIPS2})(Cp^{tBu})]_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CO_3)$. The Solid-G algorithm has been to assess the steric properties of these and previously reported mixed-sandwich complexes in the solid state and correlate these properties with the observed reactivity.

1. Introduction

The molecular non-aqueous chemistry of uranium is a growing research area and in recent decades there have been many significant advances, including the preparation of new uranium-element multiple bonds, the isolation of new oxidation states and the reduction of the strongest bonds in nature by uranium(III) complexes.[1] It would be difficult to over-emphasise the importance of the supporting ligand environment in organo-actinide chemistry and even the most established organometallic ligand environments are still surprising us with new discoveries.[2] This is well-illustrated in the isolation of the first examples of uranium(II)[3] and plutonium(II)[4] in silylated tris-cyclopentadienyl ligand environments, [(2.2.2-cryptand)K][Cp′$_3$U] (′ = $SiMe_3$) and [(2.2.2-cryptand)K][Cp″$_3$Pu]. It is notable that changing the ligand environment can change the ground