

The Nb-Cl distances in the alkyne adducts are all shorter than corresponding distances in the carbonyls. The shortest distance ($2.359 \pm 0.008 \text{ \AA}$) is found in the 16-electron complex 4 (cf. $2.495 (1) \text{ \AA}$ for Nb-Cl(terminal) in 3b). The Nb-Cl(bridge) bonds in 6 are about 0.09 \AA shorter than those in 5.²⁰ We ascribe the contraction in the alkyne adducts to increased p \rightarrow d π -donation from Cl. This in turn suggests that two carbonyls supply more electron density to Nb than one four-electron-donor alkyne and that the alkyne dimer 6 adopts the planar structure in order to maximize π -bonding to the bridging chlorides.

The facile synthesis of the low-valent Nb and Ta complexes reported here makes investigations of their chemistry feasible. In particular, the presence of easily replaceable halide ligands opens the way to new alkyl and hydride complexes.

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Supplementary Material Available: Tables of crystallographic statistics, atomic coordinates, temperature factors, bond distances and angles, and structure factor amplitudes for compounds 3b, 4, 5, and 6 (53 pages). Ordering information is given on any current masthead page.

(20) Contraction of metal-ligand(bridge) distances upon formation of a metal-metal bond has been noted previously: Curtis, M. D.; Fotinos, N. A.; Han, K. R.; Butler, W. M. *J. Am. Chem. Soc.* 1983, 105, 2686.

Preparation and Structure of $[\text{U}_2(\text{C}_6\text{Me}_6)_2\text{Cl}_7]^+$, the First Uranium(IV) Complex with a Neutral Arene in η^6 -Coordination

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Summary: The binuclear uranium(IV) compound $\{[\text{U}(\eta^6\text{-C}_6\text{Me}_6)_2\text{Cl}_2(\mu\text{-Cl})_3]\text{AlCl}_4\}$ has been prepared and its structure established by X-ray crystallography. Two uranium atoms ($\text{U}\cdots\text{U} = 3.937 (1) \text{ \AA}$) are linked by three bridging Cl atoms, and each is bonded to two terminal Cl atoms and a η^6 -hexamethylbenzene ring. The latter are essentially planar and have essentially equal C-U distances with a mean value of $2.92 [4] \text{ \AA}$. The AlCl_4^- ions are not linked to the cation.

Over the past decade the organometallic chemistry of the 4f and 5f elements has developed rapidly, and many "classical" organometallic reactions were successfully performed on actinide and lanthanide centers. Enigmatic then is the contrast between the variety of transition-metal π -complexes and the range of rare earth and actinide analogues. With one exception the latter have been restricted to the anionic π -systems allyl, cyclopentadienyl, and cyclooctatetraenyl, including the respective derivatives. The lone exception is a U(III)-benzene complex, $\text{U}(\text{C}_6\text{H}_6)(\text{AlCl}_3)_3$, where the arene ligand is bonded in an η^6 -fashion.¹ Calculations by Hoffmann and Tatsumi² on the model system U(VI)-Cp suggested a vanishingly small overlap population between the Cp ring and the uranium center; i.e., the bond appeared to be almost exclusively ionic.

As part of our effort to probe the bonding properties of f-block elements, we now report the preparation and structure of an arene complex of U(IV), $[\text{U}_2(\eta^6$ -

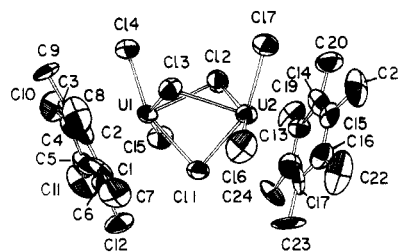


Figure 1. An ORTEP drawing of the binuclear cation, giving the atom labeling scheme. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

$\text{C}_6\text{Me}_6)_2\text{Cl}_4(\mu\text{-Cl})_3]\text{AlCl}_4^-$. The synthetic route leading to the title compound is a variation of Fischer's reductive Friedel-Crafts reaction.³ The original procedure, i.e., a melt reaction of the metal halide, AlCl_3 , hexamethylbenzene (hmb), and aluminum, in our hands, did not yield any tractable arene complexes. Typically the crude reaction products were insoluble in all but the coordinating solvents from which only UCl_4 solvates were isolated.⁴ We thus decided to separate the electrophilic addition from the reduction step. From earlier experiments we deduced that the choice of the solvent was perhaps the most important experimental parameter. Polar solvents compete with the arene through σ -donation, aromatic hydrocarbons by mass action while halogenated hydrocarbons are electrophiles in their own right, thus competing with the $\text{UCl}_3\text{-AlCl}_3$ complex. Consequently we reacted UCl_4 , AlCl_3 , and hexamethylbenzene (2 mmol, 500 mg, 2 mmol, respectively) in refluxing hexane for 12 h during which time the color and appearance of the suspension changed appreciably.⁵ The solvent was then replaced by CH_2Cl_2 in which a yellow compound was partly soluble. Addition of zinc granules resulted in a pronounced color change to red, and most of the precipitate was solubilized. After 1 h the solution was filtered through Celite and layered with hexane. Yellow crystals of the title compound formed at the walls of the Schlenk flask within 36 h while a red precipitate deposited at the bottom of the flask over the next 10 days. This latter compound is presently under investigation.

Crystals of $[\text{U}_2(\eta^6\text{-C}_6\text{Me}_6)_2\text{Cl}_4(\mu\text{-Cl})_3]^+\text{AlCl}_4^-$ consist of a well-ordered array of complex cations and tetrachloroaluminate anions.⁶ Figure 1 shows a perspective view of the cation. It is conveniently described in terms of a face-sharing bioctahedron with the hmb ligand occupying one ligand site. The bond distances, averaged over chemically equivalent bonds, are $\text{U-Cl}(\text{bridge}) = 2.75 [5] \text{ \AA}$, $\text{U-Cl}(\text{terminal}) = 2.518 [9] \text{ \AA}$, and $\text{U-C}(\text{ring}) = 2.92 [4] \text{ \AA}$. The $\text{U}\cdots\text{U}$ distance is $3.937 (1) \text{ \AA}$. The hmb moieties are highly planar with deviations from the best plane through the aromatic ring of less than 0.2 \AA (for ring carbons less than 0.05 \AA).

Naturally we should ask the question: what is the nature of the uranium-arene bond? A comparison of the $\text{U-C}(\text{ring})$ distance with those of some anionic π -ligands on U(IV) centers can be made from the data in Table I. It reveals that in our case as well as in the U(III)-benzene

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(5) All reactions were carried out under careful exclusion of air and moisture. The initially green suspension converted into a yellow precipitate.

(6) $\text{U}_2\text{Cl}_{11}\text{AlCl}_2\text{H}_{36}$: monoclinic $P2_1/c$; $a = 15.028 (4) \text{ \AA}$, $b = 8.716 (3) \text{ \AA}$, $c = 29.180 (11) \text{ \AA}$, $\beta = 93.70 (3)^\circ$, $V = 3814 (4) \text{ \AA}^3$. The structure was refined to residuals $R = 0.048$ and $R_w = 0.054$.

Table I. Comparison of U(IV)-C π -Bond Lengths

compound	U-C (mean), Å	ref
(C ₈ H ₈) ₂ U	2.65	7
[(CH ₃) ₂ C=C ₂ H ₄] ₂ U	2.66	8
Cp ₃ U(C=CPh)	2.68	9
CpU(2-MeC ₃ H ₄) ₃	2.79 (Cp), 2.66 (term), 2.80 (centr)	10
U[(Cp) ₂ CH ₂]Cl ₂ (bpy)	2.72	11
(Cp) ₄ U	2.81	12
[U(η^3 -C ₃ H ₅) ₂ (O- <i>i</i> -Pr) ₂] ₂	2.68	13
U[(CH ₃) ₂ C=C ₂ H ₄] ₂ { η^2 -CO[N(CH ₃) ₂]} ₂	2.78	14
Cp ₂ U[O ₂ C ₂ CHP(Me) ₂ (C ₆ H ₅) ₂] Fe ₂ Cp ₂ (CO) ₂] ₂	2.89	15
U(η^6 -C ₆ H ₆)(AlCl ₄) ₃	2.91	1
{[U(η^6 -C ₆ Me ₆)Cl ₂] ₂ (μ -Cl) ₃ }AlCl ₄	2.92	this work

complex the distance is longer than most of those observed with the anionic π -ligands. We interpret this as an indication for a rather weak bond, corroborating our experimental observation that it forms only in the absence of any other possible donor.

The important fact, however, is that neutral aromatic systems can bind to a uranium center strongly enough to yield isolable compounds. This implies that conditions can be engineered under which valence shell orbitals, perhaps including f orbitals or hybrids thereof, are forced to participate in some form of bonding, possibly including direct metal-metal interaction.

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Supplementary Material Available: Tables of observed and calculated structure factors, positional parameters, and anisotropic thermal parameters (17 pages). Ordering information is given on any current masthead page.

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Synthesis, Spectral Characterization, and Carbene-Transfer Reactions of CpFe(CO)₂=CH(c-C₃H₅)⁺CF₃SO₃⁻. Stabilization of Cyclopropylmethylidene by an Organometallic Fragment

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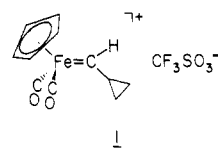
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Summary: The synthesis and spectral characterization of CpFe(CO)₂=CH(c-C₃H₅)⁺CF₃SO₃⁻ are described. The

cyclopropylmethylidene moiety may be transferred to alkenes to yield dicyclopropyl derivatives.

Iron alkylidene complexes of the type (CO)(L)CpFe=CRR'⁺ (L = CO, PR₃, P(OR)₃; R, R' = C₆H₅, H; CH₃, H; CH₃, CH₃; H, vinyl) are of synthetic interest as reagents for transfer of carbenes to alkenes.¹⁻⁷ Such species are readily and inexpensively generated, unusual stereoselectivities and enantioselectivities in their transfer reactions can be observed, and, most significantly, the Cp(L)(CO)Fe⁺ fragment is capable of stabilizing alkylidene fragments which as free carbenes or traditional carbenoids are too unstable to be synthetically useful. This latter point is illustrated by the transfer of ethylidene, propylidene, and vinyl-substituted carbenes from the corresponding Cp(CO)(L)Fe⁺ complexes to alkenes.

We report here: (1) the first generation and spectroscopic characterization of a simple cyclopropyl-substituted transition-metal carbene complex, the parent cyclopentadienyliron dicarbonyl cyclopropylmethylidene 1 (CpFe(CO)₂=CH(c-C₃H₅)⁺CF₃SO₃⁻), and (2) the utilization of this complex for the transfer of cyclopropylmethylidene to alkenes. Complex 1 is of particular interest in that



cyclopropyl-substituted carbenes and carbenoids normally undergo rapid ring expansions, fragmentations, or rearrangements⁸ and are not generally useful for the transfer of cyclopropylmethylidenes.⁹ 1 is the only alkyl-substituted derivative of the series CpFe(CO)₂=CHR⁺ to be spectroscopically characterized.

Synthesis of the Fp=CH(c-C₃H₅)⁺ complex is outlined in Scheme I. Treatment of a THF solution of Fp⁺M⁺ (Fp = CpFe(CO)₂; M = Na, K) with 1 equiv of c-C₃H₅COCl at -78 °C gives the acyl complex FpC(O)(c-C₃H₅) 2 in 65% yield.¹⁰ Reaction of 2 with (CH₃)₃O⁺BF₄⁻ in CH₂Cl₂ (25 °C, 12 h) gives Fp=C(OCH₃)(c-C₃H₅)⁺ (3).¹¹ Quenching

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