bear formal similarity with insertion of CO into Pt–O bonds of analogous platinum alkoxides.[5]

(DPPE)Pt(CH_3)[$NCH_3(C_6H_5)$], 1, rapidly reacts with acetyl chloride at 25 °C to yield (DPPE)Pt(CH_3)(Cl) and *N*-methyl-*N*-phenylacetamide. This nucleophilicity appears general; for example, 1 reacts cleanly with CD_3I to give (DPPE)Pt(CH_3)(I) and (C_6H_5)N(CH_3)(CD_3) as identified by ^1H, ^2H, and ^{31}P NMR and mass spectral analysis.[6] Complex 1 reacts analoguously to Pt(II) alkoxide complexes toward weak acids;[7] acetone, phenylacetylene, and acetonitrile all react with 1 to give *N*-methylaniline. The organometallic products, in these cases, are (DPPE)Pt(CH_3)(X) (X = CH_2COCH_3, CCPh, CH_2CN).

Our study of the equilibrium between (DPPE)PtCH_3(OCH_3) and $HNCH_3(C_6H_5)$ (eq 2) indicates the above re-

$$(\mathrm{DPPE})\mathrm{PtCH_3(OCH_3)} + \mathrm{HNCH_3(C_6H_5)} \rightleftharpoons (\mathrm{DPPE})\mathrm{PtCH_3[NCH_3(C_6H_5)]} + \mathrm{HOCH_3} \quad (2)$$

actions do not involve free amide formed by dissociation. The measured equilibrium constant of 0.8 shows the reaction to be nearly thermoneutral.[9] This information, evaluated with pK_a data, shows dissociation of methylphenylamide has an activation barrier of at least 39 kcal/mol in THF solution.[10] Interestingly, the X–H bond dissociation energies of methanol and *N*-methylaniline, combined with the thermoneutral character of eq 2 demonstrate the Pt–O bond is stronger, with respect to homolytic cleavage, than the Pt–N bond by about 16.5 kcal/mol; roughly the same as the difference between the relevant O–H and N–H bonds.[11]

In summary, we have prepared a number of platinum(II) amide complexes and have investigated their chemistry. While these species prove strong nucleophiles, they do not require dissociation of free amide to react with electrophiles. The weak Pt–N bond, relative to the Pt–O bonds, may explain the greater reactivity of late-transition-metal amide complexes than of analogous alkoxides and suggests a wealth of catalytic chemistry involving metal amides may be possible.

Acknowledgment. The technical assistance of Barry Johnson and Mike Stepro are gratefully acknowledged. We thank Andrew H. Janowicz and Thomas H. Tulip for valuable discussions.

Registry No. 1, 95465-07-9; (DMPE)PtCH_3($NC_6H_5(CH_3)$), 95465-08-0; (DPPE)PtPh(NPhCH_3), 95465-09-1; (DPPE)Pt(CH_2Ph)(NPhCH_3), 95465-10-4; (DPPE)Pt(CH_3)[NH(CH_2Ph)], 95482-63-6; (DPPE)Pt(CH_3)[C(O)$NCH_2C_6H_5$(H)], 95465-11-5; (DPPE)Pt(CH_3)(N$(CH_3)_2$), 95465-12-6; (DPPE)Pt(CH_3)[C(O)N$(CH_3)_2$], 95465-13-7; (DPPE)Pt(CH_3)(I), 27711-52-0; (C_6H_5)N(CH_3)(CD_3), 88889-00-3; (DPPE)Pt(CH_3)(CH_2COCH_3), 43210-96-4; (DPPE)Pt(CH_3)CCPh), 65310-61-4; (DPPE)Pt(CH_3)(CH_2CN), 43210-97-5; (DMPE)Pt(CH_3(Cl), 95465-14-8; (DPPE)PtCH_3(Cl), 27711-50-8; (DPPE)PtPh(Cl), 27711-51-9; (DPPE)PtCH_2Ph(Cl), 65310-81-8; (DPPE)PtCH_3(OCH_3), 82405-05-8; $HNCH_3(C_6H_5)$, 100-61-8; LiN(CH_3)(C_6H_5), 35954-01-9; LiN($CH_2C_6H_5$)(H), 38225-27-3; LiN$(CH_3)_2$, 3585-33-9; CD_3I, 865-50-9; $HNCH_3(C_6H_5)$, 100-61-8; acetyl chloride, 75-36-5; acetone, 67-64-1; phenylacetylene, 536-74-3; acetonitrile, 75-05-8; *N*-methyl-*N*-phenylacetamide, 579-10-2.

Supplementary Material Available: Additional information on the crystal structure of (DMPE)PtCH_3[$NCH_3(C_6H_5)$] and elemental analyses and spectral data on complexes reported in this paper (11 pages). Ordering information is given on any current masthead page.

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[5] (a) Bryndza, H. E.; Calabrese, J. C.; Wreford, S. S. *Organometallics* **1984**, *3*, 1603–4. (b) Bryndza, H. E. *Organometallics* **1985**, *4*, 406–408. (c) Bryndza, H. E.; Tulip, T. H.; Kietchmar, S. A., Submitted for publication in *J. Chem. Soc., Chem. Commun.* (d) Bryndza, H. E., submitted for publication in *J. Am. Chem. Soc.* (e) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199* (1), 119–135. (f) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1973**, *95*, 3030–3031. (g) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* **1979**, *175* (2), 239–255. (h) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941–3942. (i) Jones, R. F.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 58–59.

[6] We cannot, at this time, rule out a mechanism involving initial oxidative addition of the alkyl or acyl halide to the Pt(II) starting material followed by stereospecific reductive elimination; however, the singular products obtained suggest this is not the case.

[7] Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738.

[8] The equilibrium constant was measured by ^1H NMR experiments in THF-d_8 solvent. Equilibration was complete after 2 weeks at room temperature and was measured as 0.8 ± 0.1.

[9] Complex 1 can be isolated in 62% yield by combining 10 equiv of *N*-methylaniline with (DPPE)Pt(CH_3)(OCH_3). For an analogous reaction of Pt–OH with *N*-methylaniline see: Michelin, R. A.; Napoli, M. *J. Organomet. Chem.* **1979**, *175*, 239.

[10] The *upper limit* of methoxide dissociation from (DPPE)PtCH_3(OCH_3) at 25 °C in THF-d_8 has been established as 1×10^{-7} s^{-1} ($\Delta G^* > 27$ kcal/mol). From the equilibrium constant of eq 2 and the relative pK_a's of methanol and methylaniline, the rate of amide dissociation from 1 must be slower than 1×10^{-6} s^{-1} at 25 °C in THF ($\Delta G^* > 39$ kcal/mol).

[11] Bond dissociation energies of 87.5 kcal/mol (H–$NCH_3C_6H_5$) and 104 kcal/mol (H–OCH_3) were taken from: Golden, D.; McMullen, D. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. We are grateful to Professor R. G. Bergman for bringing this review to our attention.

Monomeric and Dimeric Niobium(II) and Niobium(III) Cyclopentadienyl Carbonyl and Alkyne Complexes

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Summary: Aluminum powder reduces $CpMCl_4$ (M = Nb, Ta) in the presence of 1–4 atm of CO in THF to give the dimers $Cp_2M_2(CO)_4Cl_2(\mu\text{-}Cl)_2$. In the presence of di-*p*-tolylacetylene, $Cp'NbCl_4$ is reduced by Al to give the monomeric alkyne complex $Cp'Nb(ArCCAr)Cl_2$ (**4**). The Nb(III) complexes are reduced with Na/Hg to give Nb(II) dimers with a Nb–Nb bond: $Cp'_2Nb_2(CO)_4(\mu\text{-}Cl)_2$ (**5**) and $Cp'_2Nb_2(ArCCAr)_2(\mu\text{-}Cl)_2$ (**6**). The ^{13}C NMR chemical shifts of the acetylenic carbons in **4** and **6** (216 and 214 ppm) suggest that the alkyne donates 4 electrons to the Nb atoms. The structures of **5** and **6** are dramatically different; **5** has a folded Nb_2Cl_2 core whereas **6** has a centrosymmetric structure with a planar Nb_2Cl_2 core.

We have synthesized new, low-valent organometallic complexes of Nb and Ta as part of our investigations on the chemistry of metal–metal multiple bonds.[1,2] The compounds $CpM(CO)_3Cl_2$ (1) (M = Nb, Ta), which were reported[3] to be the products of the Al reduction of $CpMCl_4$ under 1 atm of CO, offer considerable promise as convenient starting materials for metal–metal bonded complexes. Furthermore, the Al reduction procedure might be extended to give a general synthesis of Nb(III) and

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[1] (a) Review: Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, N. F. *ACS Symp. Ser.* **1981**, *No. 155*, 221–257. (b) D'Errico, J. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 4479.

[2] Metal–metal multiple bonds of Nb and Ta: (a) Sattelberger, A. P.; Wilson, R. B.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 2392 and 4179. (b) Cotton, F. A.; Hall, W. T. *Ibid.* **1980**, *19*, 2354. (c) Templeton, J. L.; McCarley, R. E. *Ibid.* **1978**, *17*, 2293.

[3] Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Organomet. Chem.* **1980**, *186*, 237.

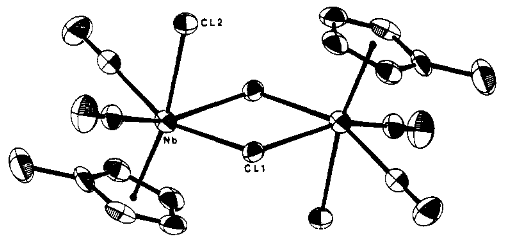


Figure 1. ORTEP plot (50% probability ellipsoids) for $Cp'_2Nb_2(CO)_4Cl_2(\mu\text{-}Cl)_2$, **3b**.

Ta(III) complexes of the type $CpMCl_2L_n$ according to eq 1. We here report the correct structure for the carbonyl

$$\underset{M = Nb,\ Ta}{CpMCl_4} + nL \xrightarrow[-AlCl_3]{Al} \underset{2}{CpMCl_2L_n} \qquad (1)$$

dichlorides of Nb and Ta, a facile synthesis of acetylene adducts of Nb(III), and their Na amalgam reductions to metal–metal bonded Nb(II) dimers.

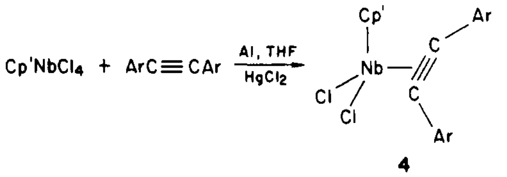
The published procedure[3] for the preparation of **1** actually gives the chloro-bridged *dicarbonyl dimers* **3**.[4] The

$$2RMCl_4 + 4CO \xrightarrow[HgCl_2]{Al,\ THF} R_2M_2(CO)_4Cl_2(\mu\text{-}Cl)_2 \qquad (2)$$

3a, M = Nb, R = C_5H_5
3b, M = Nb, R = C_5H_4Me
3c, M = Ta, R = C_5H_5

dimers **3** show two strong ν_{CO} bands in the IR and are the only carbonyl compounds detected in solution during the course of the reduction. The dimeric nature is established by a single-crystal structure determination (Figure 1). Attempts to cleave the Cl bridges with CO in refluxing THF leads to a complex disproportionation/oxygen abstraction reaction that gives rise to paramagnetic Nb_3 clusters.[5]

Diarylacetylene complexes of Nb(III) are cleanly prepared according to eq 3.[6] In contrast to the carbonyls, the acetylene adducts **4** are monomeric, both in solution and in the solid. An X-ray structure determination[7] of **4** shows it to have an overall structure similar to $Cp^*TaCl_2(PhCCPh)$.[8a] The synthesis of the acetylene adducts shown in eq 3 is much more simple than a recently reported route.[9]



$$Cp'NbCl_4 + ArC{\equiv}CAr \xrightarrow[HgCl_2]{Al,\ THF} Cp'NbCl_2(ArC{\equiv}CAr) \qquad (3)$$

4

Ar = *p*-tolyl

The chemical shift, δ 216.0, of the acetylenic carbons in **4** is in the range of values associated with four-electron-donor alkyne ligands.[10] Even with four electrons donated from the alkyne ligand, complex **4** has only a 16-electron count for Nb and exhibits some Lewis acidity.[6] That **4** is stable as a monomer, whereas the dicarbonyl fragment $CpNbCl_2(CO)_2$ dimerizes, may be due to steric effects of the alkyne ligand.

Reduction of the Nb(III) complexes **3b** and **4** with the Na amalgam in THF or toluene affords the Nb(II) dimers according to eq 4 and 5.[11,12] Compounds **5** and **6** are only

$$Cp'_2Nb_2(CO)_4Cl_4 \xrightarrow[Na/Hg]{THF} \underset{5}{Cp'_2Nb_2(CO)_4(\mu\text{-}Cl)_2} \qquad (4)$$

$$2Cp'Nb(ArC{\equiv}CAr)Cl_2 \xrightarrow[Na/Hg]{C_7H_8} \underset{6}{Cp'_2Nb_2(ArCCAr)_2(\mu\text{-}Cl)_2} \qquad (5)$$

the second examples of homometallic dimers of Nb(II). Previously reported Nb(II) or Ta(II) compounds are three heterometallic dimers of the type Cp_2NbM' (M' = $Mo(CO)_2Cp$,[13] $FeH(CO)_4$,[14] $Co(CO)_4$[15]), the phosphine complexes MCl_2L_4,[16,17] and the homometallic dimer $[CpNb(Me_4C_4H_2)(\mu\text{-}Cl)]_2$.[18]

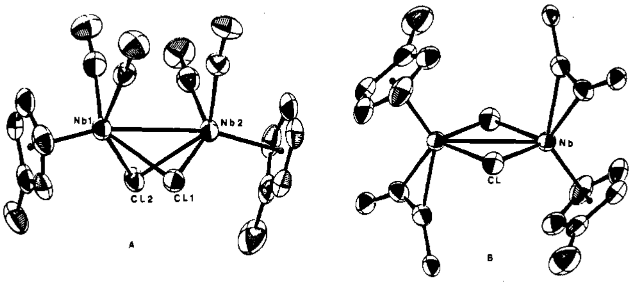


Figure 2. ORTEP plots (50% probability ellipsoids) for (a) $Cp'_2Nb_2(CO)_4(\mu\text{-}Cl)_2$, **5**, and (b) $Cp'_2Nb_2(ArCCAr)_2(\mu\text{-}Cl)_2$, **6** (Ar = *p*-tolyl). Only the ipso carbons of the aryl groups are shown.

The inner coordination spheres of **5** and **6** are shown in Figure 2. The Nb–Nb bond lengths in **5** and **6** are very similar, 3.056 (1) and 3.072 (1) Å, respectively, and are commensurate with a length expected for a Nb–Nb single bond. However, the replacement of two carbonyls by one four-electron-donor acetylene causes a dramatic change in the geometry of the Nb_2Cl_2 core. In **5**, this core is folded along the Nb–Nb bond and the carbonyls are on the same side of the folded Nb_2Cl_2 rhombus. Complex, **6**, on the other hand, is centrosymmetric with the alkyne ligands on opposite sides of the strictly planar Nb_2Cl_2 core.[19]

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[4] All new compounds reported herein gave satisfactory elemental analyses: yields for **3a** and **3b**, 60–80%, and for **3c**, 25–35%. ^1H NMR (360 MHz, C_7D_8): **3a**, δ 4.28; **3c**, δ 4.85. IR (THF, ν_{CO}, cm^{-1}): **3a** and **3b**, 2040, 1955; **3c**, 2030, 1935. CO pressures of 1–4 atm had little effect on yields or nature of products.

[5] Curtis, M. D.; Real, J., to be submitted for publication.

[6] As obtained directly from the reaction mixture, **4** contains variable amounts of coordinated THF. Repeated recrystallization from toluene gives the THF-free product in 60–70% yield: ^1H NMR (360 MHz, C_6D_6) δ 1.85 (*Me*Cp), 2.10 (*Me*Ar), 5.55, 5.79 (A_2B_2, C_5H_4Me), 7.05, 7.66 (A_2B_2, Ar); ^{13}C NMR (90.5 MHz, C_6D_6) 15.1 (*Me*Cp), 21.4 (*Me*Ar), 130.2, 112.1, 111.0 (C_5H_4Me), 129.5, 130.0, 136.5, 139.7 (Ar), 216.0 ppm (C≡C).

[7] Bond distances in **4**: Nb–C(alkyne) = 2.071 (7); C–C(alkyne) = 1.307 (7); Nb–Cl = 2.359 (8) Å. The alkyne C–C distance in **4** is 0.01–0.03 Å shorter than those observed in related Ta compounds in which the coordinated alkyne was considered to approach a RC=CR dianion (see ref 8 and 2b).

[8] (a) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387. (b) Cotton, F. A.; Hall, W. T. *Ibid.* **1980**, *19*, 2352.

[9] Belmonte, A. A.; Cloke, F. G. N.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 2365.

[10] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

[11] $Cp'_2Nb_2(CO)_4(\mu\text{-}Cl)_2$: 40% yield after recrystallization from toluene/hexane; ^1H NMR (360 MHz, C_7D_8) δ 1.69 (*Me*Cp), 4.46, 4.72 (A_2B_2, C_5H_4Me); ^{13}C NMR (90.5 MHz, C_7D_8) 14.8 (*Me*Cp), 88.9, 95.9, 116.6 ppm (C_5H_4Me) (carbonyl carbon resonances were not observed); IR (ν_{CO}, CH_2Cl_2 solution, cm^{-1}) 1990, 1910.

[12] $Cp'_2Nb_2(ArCCAr)_2(\mu\text{-}Cl)_2$ (Ar = *p*-tolyl): 60% yield after recrystallization from toluene/hexane; ^1H NMR (360 MHz, C_6D_6) δ 1.42 (*Me*Cp), 2.16 (*Me*Ar), 4.86, 5.20 (A_2B_2, C_5H_4Me), 7.73, 7.14 (A_2B_2, Ar); ^{13}C NMR (90.5 MHz, C_6D_6) 14.7 (*Me*Cp), 21.4 (*Me*Ar), 99.6, 102.1, 122.3 (C_5H_4Me), 128.8, 129.4, 137.4, 138.5 (Ar), 213.9 ppm (C≡C).

[13] Pasynskii, A. A.; Shripkin, Yu. V.; Eremenko, I. L.; Kalimnikov, V. T.; Aleksandrov, G. G.; Adrianov, V. G.; Struchkov, Yu. T. *J. Organomet. Chem.* **1979**, *165*, 49.

[14] Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979**, *18*, 136.

[15] Wong, K. S.; Scheidt, W. R.; Labinger, J. A. *Inorg. Chem.* **1979**, *18*, 1709.

[16] Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134.

[17] Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718.

[18] Bunker, M. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 85.

[19] Reference 18 states that the Nb_2Cl_2 core in $[CpNb(Me_4C_4H_2)(\mu\text{-}Cl)]_2$ is planar. No other details are provided.

Organometallics 1985, 4, 942–943

The Nb–Cl distances in the alkyne adducts are all shorter than corresponding distances in the carbonyls. The shortest distance (2.359 ± 0.008 Å) is found in the 16-electron complex 4 (cf. 2.495 (1) Å for Nb–Cl(terminal) in **3b**). The Nb–Cl(bridge) bonds in **6** are about 0.09 Å shorter than those in **5**.[20] We ascribe the contraction in the alkyne adducts to increased p → 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.

Acknowledgment. We thank the National Science Foundation for support (Grant CHE-83-5235) and Dr. W. M. Butler for collecting the crystallographic data.

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.

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(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 $[U_2(C_6Me_6)_2Cl_7]^+$, the First Uranium(IV) Complex with a Neutral Arene in η^6-Coordination

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Summary: The binuclear uranium(IV) compound $\{[U(\eta^6\text{-}C_6Me_6)Cl_2]_2(\mu\text{-}Cl)_3\}AlCl_4$ has been prepared and its structure established by X-ray crystallography. Two uranium atoms (U···U = 3.937 (1) Å) 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] Å. 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, $U(C_6H_6)(AlCl_3)_3$, where the arene ligand is bonded in an η^6-fashion.[1] Calculations by Hoffmann and Tatsumi[2] 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), $[U_2(\eta^6\text{-}C_6Me_6)_2Cl_4(\mu\text{-}Cl)_3]AlCl_4$. 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 UCl_3–$AlCl_3$ 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.

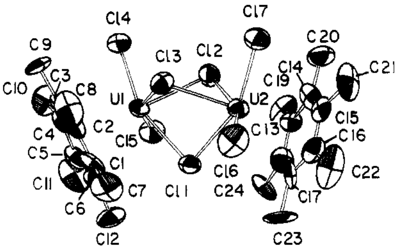

Figure 1. An ORTEP drawing of the binuclear cation, giving the atom labeling scheme. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

Crystals of $[U_2(\eta^6\text{-}C_6Me_6)_2Cl_4(\mu\text{-}Cl)_3]^+AlCl_4^-$ 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 U–Cl(bridge) = 2.75 [5] Å, U–Cl(terminal) = 2.518 [9] Å, and U–C(ring) = 2.92 [4] Å. The U···U distance is 3.937 (1) Å. The hmb moieties are highly planar with deviations from the best plane through the aromatic ring of less than 0.2 Å (for ring carbons less than 0.05 Å).

Naturally we should ask the question: what is the nature of the uranium–arene bond? A comparison of the U–C(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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(1) Cesari, M.; Pedretti, U.; Zazetta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* **1971**, *5*, 439.

(2) Tatsumi, K.; Hoffmann, R. *Inorg. Chem.* **1984**, *23*, 1633.

(3) Fischer, E. O.; Wawersik, J. *J. Organomet. Chem.* **1966**, *5*, 559.

(4) 4. Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr.*, **1984**, *C40*, 1186.

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

(6) $U_2Cl_{11}AlC_{24}H_{36}$: monoclinic $P2_1/c$; a = 15.028 (4) Å, b = 8.716 (3) Å, c = 29.180 (11) Å, β = 93.70 (3)°, V = 3814 (4) Å^3. The structure was refined to residuals R = 0.048 and R_w = 0.054.

0276-7333/85/2304-0942$01.50/0