the methyl substitution progressed, the resonance signals of the phosphorus atom and the boron atom (attached to the phosphorus) both shifted downfield, and the B–P coupling constant increased. However, the values of the chemical shifts and the coupling constants for each corresponding pair of compounds were different. The B–P coupling constant was larger, and the ^{31}P shift value was more positive for each triborane(7) adduct than for the corresponding borane(3) adduct. See Table II. These differences were considered to reflect the stronger acid strength of triborane(7), over that of borane(3), toward the phosphines. The qualitative relationship between the B–P coupling constant and the dative bond strength had been noted earlier by several investigators.[18-21]

Experimental Section

Chemicals. Laboratory stock tetraborane(10) which had been purified as described elsewhere[11] was used. Phosphine[22] and methylphosphines[23] were prepared by the literature methods. Reagent grade dichloromethane and tetrahydrofuran were stored over molecular sieves and LiAlH$_4$, respectively. Trimethylphosphine–triborane(7) was prepared by the direct, stoichiometric reaction of B$_4$H$_{10}$ with P(CH$_3$)$_3$.[5] The borane(3) adduct of P(CH$_3$)$_3$ was sublimed out from the product mixture. Volatile compounds were handled in conventional vacuum lines.

Instruments. The NMR spectra were recorded on a Varian XL-100-15 spectrometer equipped with a spin-decoupler unit (Gyrocode) and a variable-temperature control unit. The operating frequencies were 100, 40.5, and 32.1 MHz for ^{1}H, ^{31}P, and ^{11}B nuclei, respectively. The mass spectral data were obtained on an AEI MS-30 mass spectrometer operating in the electron impact mode at 70 eV.

Reactions of B$_4$H$_{10}$ with Phosphines. A 0.94-mmol sample of B$_4$H$_{10}$ was dissolved in 2 mL of CH$_2$Cl$_2$ in a 100-mL round-bottom flask equipped with a Teflon needle valve, and a 2.86-mmol sample of PH$_3$ was condensed in the flask. The flask was then allowed to warm to room temperature and stand for 2 h while the solution was agitated. The volatile components were then pumped out at 0 °C. The solvent, PH$_3$, B$_2$H$_6$, PH$_3$·BH$_3$ and B$_4$H$_{10}$ were the volatile constituents. The triborane(7) adduct, PH$_3$·B$_3$H$_7$, that remained in the flask could be distilled out slowly at room temperature. The yields were 40–60% on the basis of the amount of B$_4$H$_{10}$ used.

The reactions of B$_4$H$_{10}$ with CH$_3$PH$_2$ and (CH$_3$)$_2$PH were performed similarly, except that the reactants were mixed in 1:2 (borane:phosphine) ratios. (The use of a large excess of these phosphines resulted in the formation of the diborane(4) adducts of the phosphines. The fast reaction of (CH$_3$)$_3$P·B$_3$H$_7$ with (CH$_3$)$_3$P at room temperature to give (CH$_3$)$_3$P·BH$_3$ and B$_2$H$_4$·2P(CH$_3$)$_3$ was noted earlier.[24]) The borane(3) adducts were separated from the triborane(7) adducts by pumping on the mixtures of 0 °C and then briefly at room temperature and were identified by their ^{11}B NMR spectra. The yields of the clear liquid methylphosphine adducts of triborane(7) were virtually quantitative. The mass spectra of these three adducts were typical of triborane(7) adducts, as the highest m/e appeared at two units less than the molecular ion masses of the adducts.[11]

Reaction of THF·B$_3$H$_7$ with PH$_3$. A 0.96-mmol sample of tetrahydrofuran–triborane(7) was prepared[8] in a reaction tube (22-mm o.d. Pyrex tube), and the adduct was dissolved in diethyl ether (ca. 2 mL). A 1.25-mmol sample of PH$_3$ was condensed into the tube at −196 °C, and the tube was allowed to warm to −80 °C. The tube was then allowed to warm to higher temperatures in stepwise increments of 10 °C, while the solution was agitated continuously. At each step, the pressure of the system was monitored for the absorption of the PH$_3$ vapor by the solution. A decrease in the pressure was not observed until the mixture was warmed to 0 °C. Unchanged phosphine was fractioned out from the reaction mixture when the pressure change became undetectable. The phosphine that was recovered was 0.32 mmol, indicating that the displacement reaction was 97% complete. Upon removal of other volatile components from the reaction mixture at −23 °C, a clear liquid remained in the reaction tube. The ^{11}B NMR spectrum of this liquid in a CH$_2$Cl$_2$ solution was that of PH$_3$·B$_3$H$_7$ containing a small amount of THF·B$_3$H$_7$.[12]

Acknowledgment. The authors acknowledge support of this work by the U.S. Army Research Office through Grants DAAG 29-76-G-0120 and DAAG 29-79-C-0129.

Registry No. PH$_3$·B$_3$H$_7$, 77589-49-2; CH$_3$PH$_2$·B$_3$H$_7$, 77589-50-5; (CH$_3$)$_2$PH·B$_3$H$_7$, 77589-51-6; (CH$_3$)$_3$P·B$_3$H$_7$, 12543-29-2; B$_4$H$_{10}$, 18283-93-7; PH$_3$, 7803-51-2; CH$_3$PH$_2$, 593-54-4; (CH$_3$)$_2$PH, 676-59-5; THF·B$_3$H$_7$, 12544-89-7.

---

(20) Rudolph, R. W.; Schultz, C. W. *J. Am. Chem. Soc.* **1971**, *93*, 6821.
(21) Paine, R. T.; Parry, R. W. *Inorg. Chem.* **1972**, *11*, 1237.
(22) Gokhale, S. D.; Jolly, W. L. *Inorg. Synth.* **1967**, *9*, 56.
(23) Jolly, W. L. *Inorg. Synth.* **1968**, *11*, 124, 126.
(24) Kodama, G.; Kameda, M. *Inorg. Chem.* **1979**, *18*, 3302.

Contribution from the Institute of Nuclear Energy Research,
Lungtan, and Department of Chemistry, National Tsing Hua
University, Hsinchu, Taiwan, Republic of China

New Route for the Synthesis of Tricyclopentadienyluranium Halides

N. K. Sung-Yu, F. F. Hsu, C. C. Chang,* G. R. Her,
and C. T. Chang*

Received November 11, 1980

A facile synthetic route for UCp$_4$, UCp$_3$, U(COT)$_2$, and other related organoactinides has been achieved by the direct reaction of a fresh reactive uranium powder from electrolytic amalgamation with respective organic substrates.[1] In this work we further demonstrate the applicability of the uranium powder method to the simple synthesis of UCp$_3$X, where X = Cl, Br, and I, respectively. The uranium powder was reacted with cyclopentadiene and alkyl halides simultaneously under a mild condition to obtain the respective complexes. Previously these complexes were prepared by treating uranium tetrahalides with alkali or thalium cyclopentadienide.[2-5]

Experimental Section

Infrared spectra were obtained on a Perkin Elmer 397 IR spectrophotometer. Proton NMR spectra were recorded at 80.0 MHz on a Varian Associates FT-80A. Chemical shifts to high field of internal standard (Me$_4$Si) are given as positive. Mass spectra were obtained with use of a Varian-Mat 112 spectrometer. Gaseous products were analyzed with a Varian 3700 gas chromatograph. Elemental analyses were performed by Universal Consultant Corp. and are shown in Table I. All the operations were carried out under nitrogen in a glovebag or in an evacuated system. Organic solvents were distilled from drying agents prior to use. The starting material, uranium amalgam, was prepared as described elsewhere.[6] Thermal decomposition at 10^{-4} torr and 150 °C gave the reactive metal powder. The compound UCp$_3$ was freshly prepared prior to use as described elsewhere.[1]

Reactions of Ethyl Bromide or Iodide and Cyclopentadiene with Uranium Powder. Fifty milliliters of a benzene solution of ethyl bromide (3 mL) or ethyl iodide (3 mL) and 3 mL of freshly distilled cyclopentadiene were added to a round-bottom flask containing 5 g of freshly prepared uranium powder in an evacuated system. The reaction mixture was heated and refluxed until it turned from colorless to brown within a few minutes. After a 4-h reaction period, the gaseous products were collected and analyzed; the results are shown in Table II. The mixture was filtered; the filtrate was pumped to dryness, washed with hexane several times, and finally dried in vacuo. The solid was characterized as tricyclopentadienyluranium(IV) bromide and iodide. The yields were 85% and 90% for UCp$_3$Br and UCp$_3$I, respectively.

Reactions of Methylene Chloride or Carbon Tetrachloride and Cyclopentadiene with Fresh Uranium Powder. Fifty milliliters of a benzene solution of methylene chloride (3 mL) or carbon tetrachloride (3 mL) and 3 mL of freshly distilled cyclopentadiene were added to a flask containing 5 g of freshly prepared uranium powder in an

---

*To whom correspondence should be addressed: C.C.C., Institute of Nuclear Energy Research; C.T.C., National Tsing Hua University.

0020-1669/81/1320-2727$01.25/0 © 1981 American Chemical Society

Table I. Analytical Data for UCp$_3$X

compd	elemental^a anal.	^{1}H NMR^b	IR^c	mass^d
UCp$_3$^{35}Cl		3.48	3080 (w), 2910 (vw), 1440 (m), 1010 (s), 910 (w), 785 (vs)	468 (26.4), 433 (2.3), 403 (100), 368 (3.0), 338 (95.8), 303 (2.2), 273 (12.5)
UCp$_3$^{79}Br		3.72	3101 (w), 2925 (vw), 1440 (s), 1360 (w), 1264 (vw), 1218 (vw), 1064 (vw), 918 (m), 824–780 (vs)	512 (38.8), 447 (81.2), 382 (100), 368 (3.5), 319 (8.21), 317 (9.4), 303 (3.5)
UCp$_3$I	C 31.48 (32.14)	4.36	3100 (w), 2924 (vw), 1440 (s), 1360 (w), 1264 (vw), 1218 (vw), 1070 (m), 1016 (s), 910 (m), 826–780 (vs)	560 (47.6), 495 (64.3), 433 (76.2), 430 (83.3), 368 (100), 303 (40.5)

^{a} Calculated values in parentheses. ^{b} Me$_4$Si as internal standard. ^{c} KBr pellet. In cm^{-1}. ^{d} Relative intensities in parentheses.

Table II. Gaseous Products from Reactions of Uranium Powder with Ethyl Bromide and Cyclopentadiene and Ethyl Bromide Uranium Powder^a

reaction with HCp and C$_2$H$_5$Br: C$_2$H$_4$ (75), C$_2$H$_6$ (100), C$_4$H$_8$ (2), C$_4$H$_{10}$ (2)

reaction of C$_2$H$_5$Br: H$_2$ (4), CH$_4$ (1), C$_2$H$_4$ (100), C$_2$H$_6$ (25), C$_3$H$_6$ (1), C$_3$H$_8$ (<1), C$_4$H$_{10}$ (2)

^{a} Parentheses indicate relative intensity.

evacuated system. The reacton mixture was heated and refluxed until it turned to a deep brown. After a 3-h reaction period, the mixture was filtered; the filtrate was pumped to dryness, and the solid was transferred for sublimation. The sublimate with a yield of 40% was characterized as UCp$_3$Cl (60% yield).

Reaction of Ethyl Bromide with Uranium Powder. An excess of ethyl bromide (5 mL) was added to a flask containing 3 g of freshly prepared uranium powder in an evacuated system. The reaction mixture was stirred. Three millimoles of gaseous products were collected after an 18-h reaction period. The results are listed in Table II. The reaction mixture was filtered; the solid was extracted with water and filtered through a glass fritt. The Br/U ratio was observed to be 2.4.

Reaction of Ethyl Bromide with Tricyclopentadienyluranium. An excess of ethyl bromide (5 mL) or ethyl iodide (5 mL) was added to a solution of tricyclopentadienyluranium (2.0 g) in 50 mL of benzene in the presence of a small amount of highly reactive uranium powder in an evacuated system. The workup was the same as the previous ones. The solid was characterized as UCp$_3$Br.

Results and Discussion

The direct reaction of uranium powder with cyclopentadiene and alkyl halides probably involves an oxidative-addition mechanism. A similar pathway might be followed by the reaction of UCp$_3$ and C$_2$H$_5$Br in the presence of a small amount of uranium powder. However, what was observed in the NMR spectra was the increase of the product, UCp$_3$Br, accompanied by the corresponding decrease of UCp$_3$, and not a trace ascribable to the intermediate, C$_2$H$_5$UCp$_3$Br. The analytical data of the gaseous products from the latter are shown in Table II. Comparable quantities of ethane and ethylene were accompanied by small quantities of butane and butene. A more complicated pattern was obtained from the reaction of uranium powder with ethyl bromide. The gaseous products could be ascribed to the decomposition of a metal alkyl or/and a precursor complex from electron-transfer dehalogenation to the formation of free radicals[9,10] and to a coupling of ethyl radicals which gave butane and butene. The evolution of methane, propane, and propene is interesting; however, this observation is not ready to be interpreted.

A similar phenomenon of coupling was also found recently in the reaction of carbon tetrachloride with uranium powder, wherein a major product, C$_2$Cl$_6$, was obviously from the coupling of the ·CCl$_3$ radical.[11]

The reaction of methylene chloride or carbon tetrachloride, cyclopentadiene, and uranium powder brought forth UCp$_3$Cl with a yield of 40% and oily products ascribable to various chloro compounds. The mass spectra of UCp$_3$ and UCp$_3$Br at 70 eV appear normal; the first two Cp ligands are easily ruptured whereas the remaining one is very difficult to remove. The U–Cl and U–Br bonds are more difficult to rupture than the more covalent U–C bonds.[12] However, U–I is more easily ruptured than U–C for UCp$_3$I.

Registry No. UCp$_3$Cl, 1284-81-7; UCp$_3$Br, 67507-08-8; UCp$_3$I, 69030-40-6; UCp$_3$, 54007-00-0; C$_2$H$_5$Br, 74-96-4; C$_2$H$_5$I, 75-03-6; CH$_2$Cl$_2$, 75-09-2; CCl$_4$, 56-23-5; HCp, 542-92-7.

---

(1) Chang, C. C.; Sung-Yu, N. K.; Hseu, C. S.; Chang, C. T. *Inorg. Chem.* **1979**, *18*, 885.

(2) Marks, T. J.; Fischer, R. D. "Organometallics of the f-Elements"; D. Reidel: Dordrecht, Boston and London, 1979; p 113.

(3) Reynolds, L. T.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *2*, 246.

(4) Fischer, E. O.; Hristidu, Y. *Z. Naturforsch, Anorg. Chem., Org. Chem. B*: **1962**, *17*, 275.

(5) Marks, T. J.; Seyam, A. M.; Wachter, W. A. *Inorg. Synth.* **1976**, *16*, 147.

(6) Wang, L. C.; Lee, H. C.; Lai, W. C.; Chang, C. T. *J. Inorg. Nucl. Chem.* **1978**, *40*, 507. Wang, L. C.; Hung, H. C.; Lee, H. C.; Chang, C. T. *J. Chem. Soc., Chem. Commun.* **1975**, 124.

(7) Fischer, R. D. *J. Organomet. Chem.* **1970**, *25*, 123.

(8) Ammon, R. V.; Kannelakopulos, B.; Fischer, R. D.; Laubereau, P. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 315.

(9) Marks, T. J. *Acc. Chem. Res.* **1976**, *9*, 223.

(10) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582.

(11) Wen, T. C.; Chang, C. C.; Chuang, Y. D.; Chang, C. T., unpublished results.

(12) Anderson, M. L.; Crisler, L. R. *J. Organomet. Chem.* **1969**, *17*, 345.

Contribution from the Department of Synthetic Chemistry,
Faculty of Engineering, Kyoto University, Kyoto 606, Japan

Preparation and Characterization of Copper(I) Amides

Tetsuo Tsuda, Katsuhiko Watanabe, Kazuyoshi Miyata,
Hirotsugu Yamamoto, and Takeo Saegusa*

Received June 11, 1980

Compared to organocopper[1] and copper alkoxides,[2,3] copper amides have not been well studied. Some synthetic organic reactions involving copper amide intermediates are known.[4,5] However, isolation and characterization of copper amides derived from ordinary amines have not been reported. Recently we have prepared a unique organocopper(I) compound of mesitylcopper(I) (**1**)[6] which is thermally stable up to 100

---

(1) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 251–322.

(2) Brubaker, C. H., Jr.; Wicholas, M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 59. Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658.

(3) Whitesides, G. M.; Sadowski, J. S.; Lilburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829.

(4) Kauffmann, Th. *Angew. Chem.* **1974**, *86*, 321. Kitagawa, Y.; Oshima, K.; Yamamoto, H.; Nozaki, H. *Tetrahedron Lett.* **1975**, *1859*.

(5) Tsuda, T.; Miwa, M.; Saegusa, T. *J. Org. Chem.* **1979**, *44*, 3734.

(6) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192.

0020-1669/81/1320-2728$01.25/0