BI- AND TRIHETERONUCLEAR COMPLEXES OF URANIUM AND GROUP VI TRANSITION METALS

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Abstract—The new heterobimetallic compounds $Cp_3U[OCM(CO)_2Cp']$ containing uranium and group VI transition metals are synthesized from Cp_3UCl and $Na[M(CO)_3Cp']$ or from Cp_3UCH_3 and $H[M(CO)_3Cp']$ (M = Mo, W; $Cp = C_5H_5$; $Cp' = C_5H_5$ or C_5Me_5). In a same manner, the trimetallic $Cp_2U[OCMo(CO)_2Cp]_2$ is obtained starting from $Cp_2U(NEt_2)_2$ and $H[Mo(CO)_3Cp]$. All these complexes exhibit low CO stretching frequencies characteristic of isocarbonyl linkages between uranium and Mo or W atoms.

There is now a great interest in heterobimetallic complexes incorporating both early and late transition metals; this increase of interest is due to their potential importance in catalysis^{1,2} and organic synthesis.³ Among heterobinuclear complexes reported to date are compounds containing both group IV (Ti, Zr) and group VI (Mo, W) metals. In these compounds, the two metal atoms are not directly bonded but are linked by a bridging carbonyl ligand.^{4–8}

systems incorporating both uranium and group VI transition metal atoms.

RESULTS AND DISCUSSION

In THF solution at -50° C, Cp₃UCl reacts readily with Na[Mo(CO)₃Cp] in the molar ratio 1:1. The solution turns deep red and NaCl deposits. After removal of the solvent, 1 can be isolated in quantitative yield as a reddish brown compound but



In cyclopentadienyllanthanide series, the reaction with some group VI metallate anions has been described,⁹ but, at this time, there is no report on analogous investigations in actinide series. In an effort to develop the chemistry of cyclopentadienyluranium compounds, we have studied the condensation reactions of metallate anions $[M(CO)_3Cp']^ (M = Mo, W; Cp' = C_5H_5 \text{ or } C_5Me_5)$ with Cp_3UCl and the elimination reactions between the hydrides $H[M(CO)_3Cp']$ and Cp_3UCH_3 , Cp_3UNEt_2 and $Cp_2U(NEt_2)_2$. We report in this paper the synthesis and characterization of new bi- and triheteronuclear always containing small amounts of NaCl [equation (1)]

$$Cp_3UCl + Na[Mo(CO)_3Cp]$$

$$\xrightarrow{\text{THF}} Cp_3 U[OCMo(CO)_2 Cp]. \quad (1)$$

If pentane is added to the THF solution, 1 deposits immediately as a brown microcrystalline compound. Moreover, 1 is quantitatively obtained by a methane elimination reaction¹⁰ from Cp₃UCH₃ and H[Mo(CO)₃Cp] in heptane or toluene solutions at -50° C. In a similar manner, the bimetallic

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complexes 2 and 3 are obtained with high yields [equation (2)].

$$Cp_{3}UCH_{3} + H[M(CO)_{3}Cp']$$

$$\xrightarrow{-CH_{4}} Cp_{3}U[OCM(CO)_{2}Cp'] \quad (2)$$

$$1: M = Mo; \quad Cp' = Cp$$

$$2: M = Mo; \quad Cp' = C_{5}Me_{5}$$

$$3: M = W; \quad Cp' = Cp$$

The IR solid spectra of these compounds exhibit a very low carbonyl stretching frequency at *ca.* 1640 cm⁻¹ indicative of an isocarbonyl linkage between U and Mo (or W) atoms.^{4,5,7–10,11}

$$-U^{\oplus} \leftarrow : \bar{O} = C = \Theta M \longrightarrow U - \bar{O} = C \equiv M$$

These complexes may be considered formally to consist of the acid-base adducts of the Lewis acid Cp_3U^+ and the metallate anions $[M(CO)_3Cp']^-$. The formation of an isocarbonyl bridge preferentially to a direct metal-metal bond may be rationalized in terms of the preference of the "hard" uranium centre to form a bond with the "hard" oxygen site rather than the "soft" molybdenum or tungsten centres. This trend reflects the well known oxophilic character of actinides (or early transition metals) in relatively high oxidation state.¹²

Compounds 1, 2 and 3 are poorly soluble in non coordinating solvents such as toluene or hydrocarbons: all attempts at recrystallization lead to the formation of the hydrides H[M(CO)₃Cp'] and of unidentified uranium byproducts. A similar hydride formation has been observed with analogous titanium (or vanadium) heterobimetallic systems.¹¹ All these complexes are highly soluble in THF; the NMR spectra of the deep red solutions show a sharp C_5H_5 singlet at ca - 3.2 ppm (C_5H_5 resonance of $Cp_3UCl in THF occurs at - 3.4 ppm$); the IR spectra exhibit strong CO stretching peaks which are quite identical to those of the free carbonyl anions $[M(CO)_3Cp']^-$, thereby suggesting a substantial dissociation corresponding to an ionic structure : the companion cation is presumably [Cp₃U(THF)]⁺ [equation (3)].

$$Cp_{3}U[OCM(CO)_{2}Cp'] \xrightarrow{\text{THF}} [Cp_{3}U(THF)]^{+} + [M(CO)_{3}Cp']^{-}. \quad (3)$$

These complexes react with anhydrous HCl or CCl_4 affording in a quantitative yield Cp_3UCl and respectively $H[M(CO)_3Cp']$ and $Cl[M(CO)_3Cp']$ (identified by NMR and IR spectroscopy). Such cleavage reactions cannot thus be used as a diagnostic tool of metal-metal bonds in heterobimetallic complexes as it has been previously

claimed^{6,13} but seems to be a general feature of "early-late" transition metal binuclear compounds.^{5,8,11}

The bisdialkylamido derivative $Cp_2U(NEt_2)_2$ reacts quantitatively in heptane solution at $-70^{\circ}C$ when mixed with H[Mo(CO)₃Cp] in a 1:2 ratio. A red powder deposits and no remaining hydride or Cp_2UNEt_2 are present in the colourless supernatant heptane. This red powder is very thermally unstable and decomposes readily at room temperature affording H[Mo(CO)₃Cp] and intractable uranium products. This instability precludes recrystallization and elemental analysis. Its IR spectrum shows only three intense CO absorptions at 1900, 1740 and 1640 cm⁻¹.

The stoichiometry of the reaction and the IR data are in agreement with the trimetallic structure 4 [equation (4)].

$$Cp_{2}U(NEt_{2})_{2} + 2H[Mo(CO)_{3}Cp]$$

$$O - C \equiv Mo(CO)_{2}Cp$$

$$A$$

$$O - C \equiv Mo(CO)_{2}Cp$$

$$4$$

$$(4)$$

If dissolved in THF, even at low temperature, 4 evolves immediately with formation of $H[Mo(CO)_3Cp]$ and of the compound 1 identified by IR and NMR spectroscopy.

1 can be also obtained from Cp_3UNEt_2 in toluene or THF [equation (5)] and from the biscyclopentadienyl Cp_2UNEt_2 when performed in THF medium [equation (6)]

$$Cp_{3}UNEt_{2} + H[Mo(CO)_{3}Cp] \xrightarrow{THF} 1 + HNEt_{2} \quad (5)$$

 $Cp_2U(NEt_2)_2 + \frac{2}{3}H[Mo(CO)_3Cp]$

$$\stackrel{\text{THF}}{\longrightarrow} 1 + \text{HNEt}_2 + ? \quad (6)$$

This ligand redistribution is indicative of the greater stability of a triscyclopentadienyl versus a biscyclopentadienyl uranium moiety. This is a general trend in actinide series which reflects the tendency of the cyclopentadienyl ligands to saturate the actinide coordination sphere.^{14,15}

These studies provide further examples which illustrate the similar properties of actinides and IVA transition metal cyclopentadienyl derivatives. Both series give closely related bimetallic systems which exhibit an isocarbonyl linkage. Nevertheless, it has been recently related a series of Zr–Fe and Zr–Ru complexes¹⁶ which adopt metal-metal bonded

		Found (required) %				$vC = O(cm^{-1})$		
Compound		С	Н	М	U	(THF solution)		
1	Cp ₃ U[OCMo(CO) ₂ Cp]	39.99	3.06	13.93	35.35	1900	1740	1634
		(40.70)	(2.95)	(14.16)	(35.10)	(1899	1794	1744)
2	$Cp_3U[OCMo(CO)_2(C_5Me_5)]$	43.93	3.86	12.30	32.90	1902	1737	1645
		(44.92)	(4.02)	(12.82)	(31.81)	(1888	1785	1731)
3	Cp ₃ U[OCW(CO) ₂ Cp]	34.94	2.60	22.92	32.30	1898	1735	1635
		(36.03)	(2.61)	(24.02)	(31.07)	(1895	1795	1743)
4	Cp ₂ U[OCMo(CO) ₂ Cp] ₂	` <u> </u>	`—´	``	_	1900	1740	1640

Table 1. Analytical and IR data

structures; it seems therefore to be of interest to examine if similar attachment mode is possible in the actinide series and further work in this field is in progress.

EXPERIMENTAL

Microanalysis were by Service Central d'Analyse, CNRS (Lyon). Spectrometers: IR Perkin–Elmer 580B; spectra in nujol mulls or in THF solutions (NaCl cells), NMR Hitachi Perkin–Elmer R24 (protonated solvents) or Jeol FX100. ¹H data references to Me₄Si. All operations were performed under argon and all solvents were distilled from sodium/benzophenone under argon immediately before use.

The following complexes: Cp₃UCl,¹⁷ Cp₃UCH₃,¹⁸ Cp₃UNEt₂,¹⁹ NaM(CO)₃Cp',²⁰ HM(CO)₃Cp'²⁰ were prepared according to literature methods.

Analytical and IR data were collected in Table 1.

Preparation of Cp₃U[OCMo(CO)₂Cp]

Method A: to a stirred solution of Cp₃UCl (1.56 g) in THF (40 cm³) at -50° C was added dropwise a solution of Na[Mo(CO)₃Cp] (0.89 g) in THF (20 cm³), the reaction mixture develops immediately a deep red colour and white NaCl deposits. The solution was allowed to rise to room temperature, filtered, concentrated to *ca* 10 cm³ and pentane (30 cm³) was added. The reddish-brown powder was collected, washed with pentane and dried. Yield 2.15 g (96%).

Method B: to a stirred solution of $Cp_3UCH_3(1.12 g)$ in toluene (20 cm^3) at -50° C, was added a solution of H[Mo(CO)₃Cp] (0.615 g) in heptane (20 cm^3) . The mixture was allowed at -25° C and brown crystals deposit within *ca* 1 h. Yield 1.64 g (97%). Compounds (2) {Cp_3U[OCMo(CO)_2(C_5Me_5)]} and (3) {Cp_3U[OCW(CO)_2Cp]} were obtained in an identical manner.

Method C: to a stirred solution of $Cp_3UNEt_2(1.1 g)$ in toluene (20 cm³) at $-50^{\circ}C$ was added H[Mo(CO)₃Cp] (0.57 g) in heptane (10 cm³) and the mixture was allowed to rise to room temperature. 1 crystallises readily. Yield 1.1 g (81%).

If the reaction was performed in THF, the IR spectrum of the solution showed two strong peaks at 1898 and 1787 (very broad) cm⁻¹. The same spectrum was recorded when a small amount of HNEt₂ was added to a THF solution of 1.

Cleavage of Cp₃U[OCMo(CO)₃Cp]

HCl: To a suspension of 1 (0.5 g) in toluene (10 cm³) at -70° was added slowly a dilute solution of HCl in toluene (10 cm³). After 1 h, the brown solution was allowed to room temperature, evaporated to dryness and H[Mo(CO)₃Cp] was extracted by sublimation. The brown residue was Cp₃UCl and a very small amount of Cl[Mo(CO)₃Cp].

 CCl_4 : In the same manner, after similar treatment, the residue contains a mixture of Cp_3UCl and of $Cl[Mo(CO)_3Cp]$ in equimolecular amounts.

Preparation of $Cp_2U[OCMo(CO)_2Cp]_2$ (4)

To a stirred solution of $Cp_2U(NEt_2)_2$ (1.02 g) in heptane (20 cm³) at -70° was added H[Mo(CO)₃Cp] (0.95 g) in heptane (20 cm³). A red powder deposits readily. Yield 1.1 g (91%). 4 may be stored 24 h at $-70^{\circ}C$ without noticeable decomposition. At room temperature under argon it decomposes within *ca* 10 minutes affording quantitatively HMoCO₃Cp and an unidentified black powder.

Reaction of $Cp_2U(NEt_2)_2$ with $H[Mo(CO)_3Cp]$ in THF

To a solution of $Cp_2U(NEt_2)_2$ (1.02 g), 2×10^{-3} mol in THF (10 cm³) at room temperature, was

added dropwise a 10^{-3} mol solution of H[Mo(CO)₃Cp] in THF; the consumption of the hydride solution (1.4 cm³) was monitored by IR. After filtration, concentration and addition of pentane (30 cm³) moderately pure 1 was isolated. Yield 0.5 g (56%).

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REFERENCES

- 1. C. Masters, Adv. Organomet. Chem. 1979, 17, 61.
- K. S. Wong and J. A. Labinger, J. Am. Chem. Soc. 1980, 102, 3652.
- J. Schwartz, M. J. Loots and M. Kosugi, J. Am. Chem. Soc. 1980, 102, 1333.
- A. M. Hamilton Jr., W. S. Willis and G. D. Stucky, J. Am. Chem. Soc. 1981, 103, 4255.
- 5. J.S. Merola, R. A. Gentile, G. B. Ansell, M. A. Modrick and S. Zentz, *Organometallics* 1982, 1, 1731.
- 6. P. Renaut, G. Tainturier and B. Gautheron, J. Organomet. Chem. 1978, 150, C9.
- 7. J. C. Huffman, J. A. Marsella and K. G. Caulton, J. Am. Chem. Soc. 1981, 103, 209.

- J. A. Marsella, J. C. Huffman, K. G. Caulton, B. Longato and J. A. Norton, J. Am. Chem. Soc. 1982, 104, 6360.
- 9. A. E. Crease and P. Legzdins, J. Chem. Soc., Dalton Trans. 1973, 501.
- 10. J. R. Norton, Acc. Chem. Res. 1979, 12, 139.
- 11. C. Moise and P. Braunstein (to be published).
- J. M. Manriquez, P. J. Fagan, T. J. Marks, C. Secaur Day and V. W. Day, J. Am. Chem. Soc. 1978, 100, 7112 (and references therein).
- J. Abys and W. M. Risen Jr., J. Organomet. Chem. 1981, 204, C5.
- R. D. Ernst, N. J. Kennelly, C. Secaur Day, V. W. Day and T. J. Marks, J. Am. Chem. Soc. 1979, 107, 2656.
- 15. A. Dormond, J. Organomet. Chem. 1983, 256, 47.
- C. P. Casey, R. F. Jordan and A. L. Rheingold, J. Am. Chem. Soc. 1983, 105, 665.
- 17. T. J. Marks, A. M. Seyam and W. A. Watcher, *Inorg.* Synth. 1976, 16, 147.
- T. J. Marks, A. M. Seyam and J. R. Kolb, J. Am. Chem. Soc. 1973, 95, 5529.
- A. L. Arduini, N. M. Edelstein, J. D. Jamerson, J. G. Reynolds, K. Schmid and J. Takats, *Inorg. Chem.* 1981, 20, 2470.
- P. Braustein and J. Dehand, Bull. Soc. Chim. Fr. 1975, 1997 (and references therein).