Inorganica Chimica Acta, *139* (1987) 87–88

Reduction of Uranium(IV) Complexes Containing the Hydrotris(3,5-dimethylpyrazolyl)borate Ligand*

ISABEL SANTOS†, NOÉMIA MARQUES
and A. PIRES DE MATOS

*Departamento de Química, ICEN/LNETI,
2686 Sacavém Codex, Portugal*

The usual precursors for the preparation of organo compounds of f-elements are the metal halides. The preparation of U(III) organo compounds is usually achieved by reaction of the tetrahydrofuran adduct of U(III) chloride with the appropriate reagents. However, due to the somewhat difficult and time-consuming preparation of the halide [1], an alternative preparative route may be the reduction of an appropriate U(IV) compound.

It was previously reported that reduction of Ti and Mo complexes containing polypyrazolylborate ligands could in some cases lead to complexes in lower oxidation states [2] but in others the disruption of the molecule was observed [3].

In our laboratories we have been extensively studying U(IV) compounds with several pyrazolylborate ligands and we have also studied the reduction of two complexes containing the hydrotris(3,5-dimethylpyrazolyl)borate ligand. Here we report that the corresponding uranium(III) compounds could be isolated and no disruption was observed.

Experimental

All preparative work was carried out under dry and oxygen-free nitrogen in a glove box or using Schlenck and vacuum line techniques.

$UCl_3[HB(3,5\text{-}Me_2pz)_3]\cdot thf$ and $UCl_2[N(SiMe_3)_2][HB(3,5\text{-}Me_2pz)_3]$ were prepared as previously reported [4] (pz = pyrazolyl and thf = tetrahydrofuran). All solvents were dried and degassed before use.

$UCl_2[HB(3,5\text{-}Me_2pz)_3]$ was prepared as follows. Sodium naphthalenide (2.36 ml) in thf (0.23 mmol/ml) was added to 384 mg (0.54 mmol) of $UCl_3[HB(3,5\text{-}Me_2pz)_3]\cdot thf$ in 10 ml of thf. After stirring the mixture for 2 h the solution was centrifuged and the supernatant evaporated to dryness. The dark blue solid was washed with pentane and vacuum dried. *Anal.* Calc. for $UCl_2[HB(C_5H_7N_2)_3]$: U, 39.3; C, 29.7; H, 3.6; N, 13.9. Found: U, 39.0; C, 31.3; H, 4.0; N, 13.8%.

$UCl[N(SiMe_3)_2][HB(3,5\text{-}Me_2pz)_3]$ was prepared by adding 1.38 ml of $NaC_{10}H_8$ in thf (0.28 mmol/ml) to 300 mg (0.39 mmol) of $UCl_2[N(SiMe_3)_2][HB(3,5\text{-}Me_2pz)_3]$ in 10 ml of thf. An immediate colour change from green to wine-red was observed. The supernatant was treated as described above and the red complex analysed. *Anal.* Calc. for $UCl[N(SiMe_3)_2][HB(C_5H_7N_2)_3]$: C, 34.5; H, 5.5; N, 13.4. Found: C, 34.6; H, 5.4; N, 12.5%.

The electronic spectra in benzene and tetrahydrofuran were identical (nm): 900(s), 917(s), 1009(w), 1036(w), 1069(w), 1186(m), 1200(sh), 1225(m).

Infrared spectrum (Nujol mull): ν(B–H) 2540 cm^{-1}, ν(U–Cl) 255 cm^{-1}.

Results and Discussion

The addition of equimolar amounts of $NaC_{10}H_8$ in thf to a green solution of $UCl_3[HB(3,5\text{-}Me_2pz)_3]\cdot thf$ in thf gave an immediate reaction and a dark blue solution was obtained. The electronic absorption spectrum of this solution was characteristic of a U(III) species and gave the same pattern as observed previously for the U(III) complex $UCl_2[HB(3,5\text{-}Me_2pz)_3]$ prepared by a different way [5]. Work-up of this solution led to a blue solid, the IR and ^1H NMR spectra of which were identical with the results we had obtained before [5].

Using as starting material the U(IV) complex $UCl_2[N(SiMe_3)_2][HB(3,5\text{-}Me_2pz)_3]$ and following the same procedure as described above, the red complex $UCl[N(SiMe_3)_2][HB(3,5\text{-}Me_2pz)_3]$ was isolated. The ^1H NMR spectrum of this complex in thf-d_8 gave only a very broad signal at 4.9 ppm. However, upon lowering the temperature, new resonances appeared and by 220 K the low temperature limiting spectrum could be reached and showed ten resonances at 20.7(3H), 19.5(3H), 16.4(6H), 6.5(6H), −9.4(3H), −12.1(6H), −12.7(1H), −15.2(2H), −52.1(3H) and −56.7(6H). Thus the deceptive spectrum at room temperature must be due to some exchange process.

Although a complete assignment could not be made, from the intensity ratios of the bands the signals at −12.7(1H) and −15.2(2H) must be due to the H(4) protons of the pyrazolyl rings. This indicates that only two of the three pyrazolyl rings are equivalent and therefore the resonances due to the CH_3 protons of the $[HB(3,5\text{-}Me_2pz)_3]$ ligand should have an intensity ratio 3:3:6:6. Bearing this in mind, the

---

*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

†Author to whom correspondence should be addressed.

0020-1693/87/$3.50

other signals with intensity ratios of 3:3:6:6 appear to belong to the protons of the hexamethyldisilylamide group. The above observations indicate that the pyrazolyl ligand may have fluxional behaviour and that rotation about the U–N bond is hindered. Thus this complex is sterically more congested than the complex $UCl_2[HB(3,5\text{-}Me_2pz)_3]$, for which the ^1H NMR spectrum shows a pattern indicating equivalence of all the pyrazolyl rings [5].

References

1 D. C. Moody, A. J. Zozulin and K. V. Salazar, *Inorg. Chem., 21,* 3856 (1982).
2 J. K. Kouba and S. S. Wreford, *Inorg. Chem., 15,* 2313 (1976).
3 J. A. McCleverty, *Chem. Soc. Rev., 12,* 331 (1980).
4 J. Marçalo, N. Marques, A. Pires de Matos and K. W. Bagnall, *J. Less-Common Met., 122,* 219 (1986).
5 I. Santos, N. Marques and A. Pires de Matos, *J. Less-Common Met., 122,* 215 (1986).