Journal of Organometallic Chemistry, 99 (1975) C19—C20

Preliminary communication

TRIMETHYLSILYLMETHYL AND METHYL COMPOUNDS OF MANGANESE, COBALT AND URANIUM

RICHARD ANDERSEN, ERNESTO CARMONA-GUZMAN, KONSTANTINOS MERTIS, ELIN SIGURDSON and GEOFFREY WILKINSON*
Inorganic Chemistry Laboratories, Imperial College of Science and Technology, London SW7 2AY (Great Britain)

(Received July 28th, 1975)

Summary

Thermally stable alkylmanganese(II) compounds, $Mn(CH_2R)_2$ R = $SiMe_3$, CMe_3 and CMe_2Ph have been isolated; and oxidation with dioxygen shown to give unstable green alkylmanganese(IV) compounds; lithium alkylate anions of manganese(II), cobalt(II) and uranium(IV) have also been isolated as tetrahydrofuran or tetramethylethylenediamine solvates, the uranium compounds, e.g. $Li_2[U(CH_2SiMe_3)_6](tmed)_7$ being the first uranium complexes with more than one metal to carbon σ-bond.

It has been noted that peralkyl-transition metal compounds may be obtained on occasion only when the products of interaction of the metal halide and lithium or Grignard reagents are exposed to oxygen, advantitiously or deliberately [1]. The former may well be true for the synthesis [2] of metal norbornyls in high oxidation states.

In attempts to produce alkylmanganese(IV) compounds other than the tetranorbornyl [2] we have isolated from the reaction of manganeous chloride and trimethylsilylmethyl, neopentyl and neophyl reagents, the crystalline alkyls $Mn(CH_2R)_2$, R = $SiMe_3$, CMe_3 and CMe_2Ph, respectively**. The only other binary alkyl is $Mn(CH_3)_2$ [3], but its insolubility in solvents with which it does not react, and its thermal and oxidative instability limit its study. The above alkyls are readily soluble in ether and hydrocarbon solvents and are thermally stable to over 100 °C. The trimethylsilylmethyl compound with tetramethylethylenediamine (tmed) form the stable adduct $(Me_3SiCH_2)_2Mn(tmed)$. Oxidation of solutions of the alkylmanganese(II) compounds with excess of reagent by molecular oxygen gives green

---

*To whom correspondence should be addressed.

**Good analytical data for this and other compounds noted here were obtained in addition to supporting spectroscopic data.

sublimable and petroleum soluble products that are thermally and photochemically labile. From the similarity to the tetranorbornyl and from electron spin resonance studies these appear to be the $Mn(CH_2R)_4$ species. Attempts to oxidise methylmanganese compounds under similar conditions failed but we have isolated $[LiS]_2[Mn(CH_3)_4]$ (S = tetrahydrofuran and tmed); the red crystalline tmed complex is stable to 150 °C and soluble in benzene. Some poorly characterised lithium salts, $Li[MnR_3]$, have been reported [4].

Although norbornyl cobalt(IV) exists [2,5] oxidation again fails for methyl- and trimethylsilylmethyl-cobalt but we can isolate the crystalline salts $[Li(tmed)]_2[CoR_4]$ ($R = CH_3$, blue, $R = CH_2SiMe_3$, red-brown), by interaction of cobalt(II) chloride and LiR in ether followed by addition of tmed. The trimethylsilylmethyl compound is quite stable thermally.

Attempts to synthesise stable alkyluraniums in this laboratory* by interaction of UCl_4, UCl_6 and $U(OC_2H_5)_5$ with alkyllithiums and alkylmagnesiums failed, although petroleum solutions of an unstable trimethylsilylmethyl compound could be obtained. Marks and Seyan [6] also failed, as did their attempts to stabilize alkyluraniums by addition of 2,2′-dipyridyl.

Since the formation of anionic species clearly seems a useful alternative to the addition of neutral ligands as a means of saturating the coordination sites of the metal, we have treated uranium(IV) chloride in ether with an excess of various lithium reagents such as trimethylsilylmethyllithium, methyllithium and 2-benzyldimethylaminelithium [7]. Solvated lithium salts of uranium(IV) with a Li/U ratio 2/1 are obtained. The green crystalline salt $Li_2U(CH_2SiMe_3)_6(tmed)_7$ and the red-purple $Li_2U(C_9H_{12}N)_6(tmed)_7$ are the first alkyluranium compounds with more than one metal to carbon σ-bond, the only other alkyls being of the type $(\eta^5\text{-}C_5H_5)_3UR$ [8]. Both are reasonably stable at room temperature but the methyl decomposes at about 0 °C. The trimethylsilylmethyltetrahydrofuran solvate is paramagnetic (μ_{eff} 2.7 BM) but in tetrahydrofuran gives a ^1H NMR spectrum with single broad resonances at τ11.2(9) and 19.6(2). There seems now no reason why numerous other alkylate anions of uranium and the actinide, as well as lanthanide, elements with multiple M—C σ-bonds cannot be isolated.

References

1 W. Mowat, A. Shortland, G. Yagupsky, N.J. Hill, M. Yagupsky and G. Wilkinson, J. Chem. Soc. Dalton, (1972) 533; L. Galyer, K. Mertis and G. Wilkinson, J. Organometal. Chem., 85 (1975) C37; K. Mertis, D.H. Williamson and G. Wilkinson, J. Chem. Soc. Dalton, (1975) 607.
2 B.K. Bower and H.G. Tennent, J. Amer. Chem. Soc., 94 (1972) 2512.
3 C. Beerman and K. Clauss, Angew. Chem., 71 (1959) 627.
4 R. Riemschneider, H.-G. Kassahn and W. Schneider, Z. Naturforschg. B, 15 (1960) 547.
5 B.K. Bower, M. Findlay and J.C.W. Chien, Inorg. Chem., 13 (1974) 759.
6 T.J. Marks and A.M. Seyan, J. Organometal. Chem., 67 (1974) 61.
7 C.T. Viswanathan and C.A. Wilkie, J. Organometal. Chem., 54 (1973) 1.
8 T.J. Marks, A.M. Seyan and J.R. Kolb, J. Amer. Chem. Soc., 95 (1973) 5529; G.W. Halstead, E.C. Baker and K.N. Raymond, J. Amer. Chem. Soc., 97 (1975) 3049.

---

*By Professor T.M. Brown (Arizona State University), A.J. Shortland and L. Galeyer.