Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

TETRAKIS(PENTACARBONYLMANGANESE)URANIUM

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(Received August 10th, 1970)

SUMMARY

The preparation and properties of $U[Mn(CO)_5]_4$, the first reported complex containing a uranium–transition metal, bond, are described.

INTRODUCTION

The organometallic chemistry of the actinides has been receiving much attention recently[1], and cyclopentadienyl derivatives of thorium[1], protactinium[1], uranium[1,2], neptunium[1,3], plutonium[1], americium[1,4], curium[5], berkelium[6,7], and californium[6] have been described. Other recent studies have resulted in the syntheses of bis(cyclooctatetraene)thorium[8] and -uranium[9], and of tetraallyluranium[10]. However, no reports of any complexes of the actinides containing either homo- or hetero-nuclear metal–metal bonds have appeared.

EXPERIMENTAL

All reactions and operations were carried out with the strict exclusion of oxygen; precautions taken included degassing solvents, followed by saturation with nitrogen. Solid materials were handled in a conventional nitrogen-filled dry box.

A solution of sodium pentacarbonylmanganate [from $Mn_2(CO)_{10}$ (2.3 g, 11.8 mmoles) in tetrahydrofuran (50 ml) and excess sodium amalgam] was treated with a solution of uranium tetrachloride (1.0 g, 2.95 mmoles) in the same solvent (30 ml). After 3 h at room temperature, the resulting deep red solution was evaporated to dryness, and the residue was extracted with acetone (15 ml). Addition of light petroleum (30 ml) to the filtered extract, followed by slow evaporation of the acetone under reduced pressure, caused separation of a bright orange solid. The product was filtered, washed with light petroleum, and dried in vacuum, to give pure $U[Mn(CO)_5]_4$ (1.35 g, 50%) decompn. 180° [Found: C, 23.89; H, 0.0; Cl, 0.0; Mn, 23.55; O, 31.05; mol. wt., 905 (acetone). $C_{20}Mn_4O_{20}U$ calcd.: C, 23.58; H, 0.0; Cl, 0.0; Mn, 21.62; O, 31.44%; mol. wt., 1018.] IR spectrum (acetone): ν(CO) bands at 2043 m, 2031 m, 2007 s, 1969 s (br), 1936 m, 1895 m, 1889 (sh), 1863 m cm^{-1}.

DISCUSSION

The reaction between uranium tetrachloride and the sodium derivative of decacarbonyldimanganese gives an extremely air-sensitive bright orange solid, which can be isolated in about 50% yield. The new complex was characterised as $U[Mn(CO)_5]_4$ by analysis, osmometric molecular weight determinations, and some chemical reactions. No parent ion was found in the mass spectrum, and it appears that some decomposition occurs in the spectrometer; the only ions which could be unequivocally identified were members of the series $[Mn(CO)_n]^+$ ($n = 0$–5), $[Mn_2(CO)_n]^+$ ($n = 0$–5); ions at m/e 238, 293 and 331 are tentatively assigned to $[U]^+$, $[UMn]^+$ and $[UMn(CO)]^+$, respectively.

Exposure of the complex to air resulted in rapid darkening, and washing the solid with light petroleum gave bright yellow solutions containing $Mn_2(CO)_{10}$; the fate of the uranium was not determined. Treatment of the complex with a solution of bromine in carbon tetrachloride resulted in the formation of $Mn(CO)_5Br$ and UBr_4, in 70% and 99%, respectively, of the amounts required for the reaction:

$$U[Mn(CO)_5]_4 + 4\ Br_2 \rightarrow UBr_4 + Mn(CO)_5Br$$

A solution of the complex in chloroform shows only the $\nu(CO)$ bands of $Mn(CO)_5Cl$ by the time the IR spectrum can be taken. The complex is moderately soluble in acetone, but the $\nu(CO)$ bands slowly change.

Similar reactions between $[Re(CO)_5]^-$ and $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and UCl_4 gave $Re(CO)_5Cl$ and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, respectively, as the only isolable products. With $[Co(CO)_4]^-$, $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$, unstable complexes containing uranium–transition metal bonds were formed, but these have not yet been fully characterised.

ACKNOWLEDGEMENT

One of us (R.L.B.) thanks the SRC for a Research Studentship.

REFERENCES

1 H. GYSLING AND M. TSUTSUI, *Advan. Organometal. Chem.*, 9 (1970) 361, and references therein.
2 R. V. AMMON, B. KANELLAKOPULOS AND R. D. FISCHER, *Radiochim. Acta.*, 11 (1969) 162.
3 R. D. FISCHER, P. LAUBEREAU AND B. KANELLAKOPULOS, *Z. Naturforsch. A*, 24 (1969) 616.
4 R. PAPPALARDO, W. T. CARNALL AND P. R. FIELDS, *J. Chem. Phys.*, 51 (1969) 842.
5 P. G. LAUBEREAU AND J. H. BURNS, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 59.
6 P. G. LAUBEREAU AND J. H. BURNS, *Inorg. Chem.*, 9 (1970) 1091.
7 P. G. LAUBEREAU, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 611.
8 A. STREITWIESER AND N. YOSHIDA, *J. Amer. Chem. Soc.*, 91 (1969) 7528.
9 A. STREITWIESER AND E. MÜLLER-WESTERHOFF, *J. Amer. Chem. Soc.*, 90 (1968) 7364.
10 G. LUGLI, W. MARCONI, A. MAZZEI, N. PALADINO AND U. PEDRETTI, *Inorg. Chim. Acta.*, 3 (1969) 253.