Journal of Organometallic Chemistry, 146 (1978) C43—C45

Preliminary communication

BIS(PHENYLETHYNYL)YTTERBIUM - A NOVEL ORGANOLANTHANIDE.

G.B. Deacon and A.J. Koplick

Chemistry Department, Monash University, Clayton, Victoria 3168 (Australia)

(Received December 16th, 1977)

Summary

Reaction of bis(phenylethynyl)mercury with ytterbium metal and of bis(pentafluorophenyl)ytterbium with phenylacetylene yields bis(phenylethynyl)-ytterbium, which has been isolated without supporting ligands and is exceptionally air-sensitive. An associated structure is likely.

Known phenylethynyl-lanthanides and -actinides belong to the classes $(\eta\text{-}C_5H_5)_3MCCPh$ (M = actinide) and $(\eta\text{-}C_5H_5)_2M'CCPh$ (M' = lanthanide) [1 - 4], except for $\eta\text{-}C_5H_5Ho(CCPh)_2$ [3]. In all cases the M — CCPh bond is stabilised by the η-cyclopentadienyl groups [4]. We now report the preparation of a phenylethynyllanthanide without supporting ligands, viz. bis(phenylethynyl)-ytterbium. The synthetic methods involve transmetallation, which has only recently been applied to organolanthanides [5], and a novel ligand exchange reaction.

Reaction of approximately equimolar amounts of bis(phenylethynyl)mercury and ytterbium metal in dry tetrahydrofuran at room temperature under rigorously purified nitrogen resulted in precipitation of mercury and formation of a very dark purple solution of bis(phenylethynyl)ytterbium.

$$(PhCC)_2Hg + Yb \rightarrow (PhCC)_2Yb + Hg\downarrow$$

After filtration, addition of petroleum ether and cooling gave purple-black crystals of *unsolvated* bis(phenylethynyl)ytterbium with satisfactory analyses (C,H,Yb) in 22% yield (cf. isolation of bis(pentafluorophenyl)ytterbium as $(C_6F_5)_2Yb(THF)_4$ [5]). The compound was also synthesized by reaction of bis(pentafluorophenyl)ytterbium with phenylacetylene in dry tetrahydrofuran.

$$(C_6F_5)_2Yb + 2PhCCH \rightarrow (PhCC)_2Yb + 2C_6F_5H$$

Crystals obtained by this route (yield 41%) were somewhat less pure than those prepared by transmetallation.

Bis(phenylethynyl)ytterbium is exceptionally sensitive to water and oxygen, but is indefinitely stable at room temperature under purified nitrogen. Thermal decomposition without melting was observed at *ca.* 200°C in a sealed tube. The infrared spectrum confirmed that the compound does not contain tetrahydrofuran, and showed $\nu(C \equiv C)$ at *ca.* 2040 – 2020 cm^{-1} (slight variations in position and intensity were observed between samples), lowered from values for phenylacetylene (2112 cm^{-1} [6]) and bis(phenylethynyl)-mercury (2149 and 2117 cm^{-1} [7]). The chemical shifts of the aromatic protons in tetrahydrofuran-d_8 (7.12, 7.38 and 7.71 p.p.m. downfield from external tetramethylsilane) are as expected [8] for a phenylethynyl derivative of a diamagnetic metal ion (Yb^{2+}, $4f^{14}$). Paramagnetic f block metal ions cause marked shifts of proton resonances [2,9] (e.g. see data [2] for $(\eta\text{-}C_5H_5)_3UCCPh$).

Acidolysis of bis(phenylethynyl)ytterbium gave phenylacetylene

$$(PhCC)_2Yb + H_2SO_4 \rightarrow YbSO_4 + 2PhCCH$$

containing styrene (*ca.* 20%) and a little ethylbenzene (*ca.* 1%). The PMR spectrum of $(PhCC)_2Yb$ showed no features indicative [10] of a styrylorganometallic impurity, which would yield styrene on hydrolysis, hence the source of styrene is probably hydrogenation during treatment with acid. In confirmation, acidolysis with sulphuric acid-d_2 gave a significant amount of *trideutero*styrene, consistent with partial hydrogenation.

$$2(PhCC)_2Yb + 3D_2SO_4 \rightarrow 3PhCCD + PhCDCD_2 + Yb_2(SO_4)_3$$

Since a coordination number of two is highly improbable in an organolanthanide [4,11], an associated structure is likely for $(PhCC)_2Yb$. Molecular weights indicative of trimeric — tetrameric species were obtained by boiling point elevation in tetrahydrofuran. Although the error is probably large owing to partial decomposition during the measurements (*ca.* 70% of the expected phenylacetylene was obtained on acidolysis after the molecular weight determination), substantial association is clearly indicated. This may involve either σ-bridging through the α-carbon atom, as in $[Me(MeCC)BeNMe_3]_2$ [12], or, more likely, π-bonding between the triple bond [see lowering of $\nu(C \equiv C)$, above] and ytterbium, as observed in phenylethynylcopper [13].

Acknowledgement

We are grateful to the Australian Research Grants Committee for support, to Dr. D.J. Knowles, Preston Institute of Technology, for gc/ms facilities, and to Dr. T. Mole, Division of Tribophysics, C.S.I.R.O., for helpful discussions.

References

1. T.J. Marks, Acc. Chem. Res., 9 (1976) 223; M. Tsutsui, N. Ely, and R. Dubois, Acc. Chem. Res., 9 (1976) 217; T.J. Marks, J. Organometal. Chem., 138 (1977) 157; M. Tsutsui, N. Ely, A.E. Gebala, and J.L. Atwood, Ann. N.Y. Acad. Sci., 239 (1974) 160.
2. A.E. Gebala and M. Tsutsui, J. Amer. Chem. Soc., 95 (1973) 91.
3. N.M. Ely and M. Tsutsui, Inorg. Chem., 14 (1975) 2680.
4. E.C. Baker, G.W. Halstead, and K.N. Raymond, Structure and Bonding, 25 (1976) 23.
5. G.B. Deacon and D.G. Vince, J. Organometal. Chem., 112 (1976) C1; G.B. Deacon, W.D. Raverty and D.G. Vince, J. Organometal. Chem., 135 (1977) 103.
6. G.W. King and S.P. So, J. Mol. Spectros., 36 (1970) 468.
7. G.E. Coates and C. Parkin, J. Chem. Soc., (1962) 3220.
8. E.A. Jeffrey and T. Mole, J. Organometal. Chem., 11 (1968) 393.
9. T.J. Marks, A.M. Seyam, and J.R. Kolb, J. Amer. Chem. Soc., 95 (1973) 5529; K.O. Hodgson, F. Mares, D.F. Starks, and A. Streitwiesser, J. Amer. Chem. Soc., 95 (1973) 8650.
10. H. Shinozaki, M. Kubota, O. Yagi and M. Tada, Bull. Chem. Soc. Japan, 49 (1976) 2280.
11. S.P. Sinha, Structure and Bonding, 25 (1976) 69.
12. B. Morosin and J. Howatson, J. Organometal. Chem., 29 (1971) 7.
13. P.W.R. Corfield and H.M.M. Shearer, unpublished results in M.L.H. Green, Organometallic Compounds, 3rd. Edn., Vol. 2, (Methuen, London 1968) pp. 274, 275.