Journal of Organometallic Chemistry, 202 (1980) C71—C72
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

CYCLOPENTADIENYLZINC DERIVATIVES OF MANGANESE, MOLYBDENUM AND TUNGSTEN: THE FIRST EXAMPLES OF STABLE ORGANOZINC-TRANSITION METAL COMPOUNDS

P.H.M. BUDZELAAR, J. BOERSMA and G.J.M. VAN DER KERK
Laboratory for Organic Chemistry, State University, Utrecht (The Netherlands)
(Received September 15th, 1980)

Summary

The preparation of four cyclopentadienylzinc transition metal compounds is described. These compounds are stable with respect to symmetrization into dicyclopentadienylzinc and zinc bis(transition metal) compounds.

Symmetric zinc-transition metal compounds (containing zinc directly bound to two transition metal atoms) are well-known [1—3], but attempts to prepare the asymmetric organozinc-transition metal compounds have so far met with little success. In all cases, the initially formed products of the type RZnTm disproportionated according to

$$2\ RZnTm \rightarrow R_2Zn + ZnTm_2 \quad (Tm = \text{transition-metal containing group})$$

Recently [4], the presence of $C_6H_5ZnMo(C_5H_5)(CO)_3$ in solutions of $Zn[Mo(C_5H_5)(CO)_3]_2$ and excess $(C_6H_5)_2Zn$ was demonstrated by proton NMR spectroscopy, but the compound could not be isolated.

We now report the preparation of four stable organozinc transition metal compounds, viz.: $C_5H_5ZnMn(CO)_5$, $C_5H_5ZnMo(C_5H_5)(CO)_3$, $(C_5H_5Zn)_2Mo(C_5H_5)_2$ and $(C_5H_5Zn)_2W(C_5H_5)_2$. All are obtained in quantitative yield when the parent transition metal hydride is treated with an excess of (insoluble) Cp_2Zn in benzene at room temperature:

$$Cp_2Zn + TmH \rightarrow CpZnTm + CpH$$

$$(Tm = Mo(Cp)(CO)_3,\ Mn(CO)_5,\ \tfrac{1}{2}MoCp_2,\ \tfrac{1}{2}WCp_2)$$

The manganese compound, however, is more conveniently prepared by refluxing a suspension of Cp_2Zn and $Zn[Mn(CO)_5]_2$ (from Zn and $Mn_2(CO)_{10}$ [2]) n benzene for 30 minutes.

TABLE 1

^1H AND ^{13}C CHEMICAL SHIFTS (IN C_6D_6, RELATIVE TO INTERNAL TMS)

Compound	^1H		^{13}C		
	Cp(Zn)	Cp(Tm)	Cp(Zn)	Cp(Tm)	CO(Tm)
$CpZnMn(CO)_5$	6.12	—	103.8	—	216.1
$CpZnMo(Cp)(CO)_3$	6.37	4.58	104.2	86.9	226.8
$(CpZn)_2MoCp_2$	6.41	3.88	105.4	65.3	—
$(CpZn)_2WCp_2$	6.39	3.81	105.3	60.8	—

The title compounds* are thermally stable solids, soluble in benzene; molecular weights determined by ebulliometry in this solvent showed them to be monomeric. Proton and ^{13}C NMR data are presented in Table 1.

Investigations into the factors governing the degree of stability of organozinc-transition metal compounds with respect to symmetrization are currently in progress.

References

1 B.R. Francis, M.L.H. Green, T. Luong-thi, G.A. Moser, J. Chem. Soc., Dalton, (1977) 1339.
2 J.M. Burlitch, J. Chem. Soc., Chem. Commun., (1968) 887.
3 N.A.D. Carey and J.G. Noltes, J. Chem. Soc., Chem. Commun., (1968) 7471.
4 J.N. StDenis, W. Butler, M.D. Glick and J.P. Oliver, J. Organometal. Chem., 129 (1977) 1.

*Satisfactory analytical data were obtained for all the compounds.