

Preliminary communication

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

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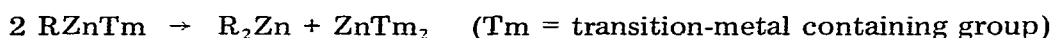
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(Received September 15th, 1980)

Summary

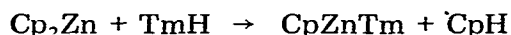
The preparation of four cyclopentadienylzinc transition metal compounds is described. These compounds are stable with respect to symmetrization into di-cyclopentadienylzinc and zinc bis(transition metal) compounds.

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



Recently [4], the presence of $C_5H_5ZnMo(C_5H_5)(CO)_3$ in solutions of $Zn[Mo(C_5H_5)(CO)_3]_2$ and excess $(C_5H_5)_2Zn$ 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:



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

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]) in benzene for 30 minutes.

TABLE 1

¹H AND ¹³C CHEMICAL SHIFTS (IN C₆D₆, RELATIVE TO INTERNAL TMS)

Compound	¹ H		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) ₂ MoCp ₂	6.41	3.88	105.4	65.3	—
(CpZn) ₂ WCp 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 ¹³C NMR data are presented in Table 1.

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

References

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*Satisfactory analytical data were obtained for all the compounds.