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Preliminary communication

AN INTRIGUING PLUMBYLENE: BIS[2-(DIMETHYLAMINOMETHYL)-PHENYL] LEAD

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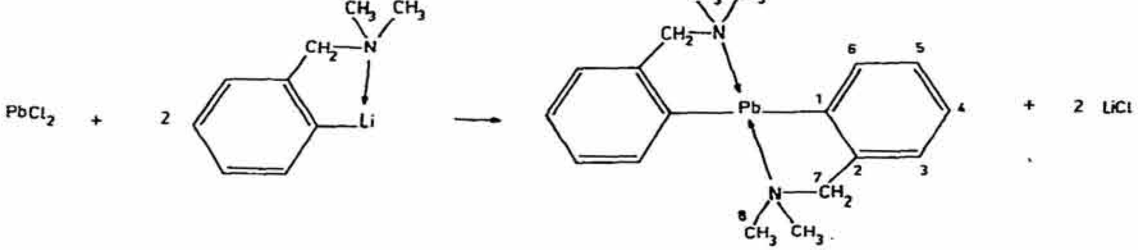
Summary

The diaryllead compound bis[2-(dimethylaminomethyl)phenyl]lead has been isolated and characterized. The monomeric composition of the plumbylene has been established by cryoscopic measurements. Comparison of the ^{1}H and ^{13}C NMR data of this plumbylene with those of tetrakis[2-(dimethylaminomethyl)-phenyl]lead reveals striking differences.

The only known bivalent organolead compounds containing lead—carbon bonds are bis(cyclopentadienyl)lead [1,2], bis(methylcyclopentadienyl)lead [3] and bis[bis((trimethylsilyl)methyl]lead [4]. The first report of the synthesis of diaryllead compounds as monomeric species appeared in 1922 by Krause and Reissaus [5], but later workers failed to repeat the experiments [6—9].

We now report our investigation of the compound bis[2-(dimethylamino-methyl)phenyl]lead. As diarylplumbylenes are thought to show a lower tendency to polymerise and lower reactivity if the aryl groups contain substituents causing steric hinderance, we used the ligand 2-(dimethylaminomethyl)-phenyl [10—12].

The reaction of lead(II) chloride with two equivalents of 2-(dimethylamino-



methyl)phenyllithium was carried out in THF at −50°C. On evaporation bis-[2-(dimethylaminomethyl)phenyl]lead was isolated in 90% yield as a white powder, soluble in THF, $CHCl_3$ and benzene (yellow solutions). All manipulations were carried out in Schlenk glassware in an oxygen- and moisture-free nitrogen atmosphere. The 2/1 aryl/lead ratio in the plumbylene agrees well with the lead content as indicated by elemental analysis: found 43.0% (calcd. 43.6%). Cryoscopic measurements in benzene on two samples of the plumbylene showed the average molecular weight to be 490 ($C_{18}H_{24}N_2Pb$, calcd. 475.6). On the basis of these results we conclude that the compound is monomeric in benzene, and that alternative formulations as telomeric $(Ar_2Pb)_p$ or cyclic $(Ar_2Pb)_q$ can be ruled out.

TABLE 1

^{1}H CHEMICAL SHIFTS^{a} AND ^{207}Pb—^{1}H COUPLING CONSTANTS^{b} OF [2-(DIMETHYLAMINOMETHYL)PHENYL]$_n$ LEAD (n = 2,4)^{c}

n	H(3,4,5)	H(6)	H(CH_2)	H(CH_3)
2	6.9—7.4 (—)^{d}	7.97 (27)	3.79 (6)	2.46
4	7.2—7.6 (—)^{d}	8.0 (118)	3.68 (13)	2.00

^{a}In ppm; reference TMS. ^{b}In Hz; in parentheses. ^{c}In $CDCl_3$. ^{d}Not observed.

TABLE 2

^{13}C CHEMICAL SHIFTS^{a} AND ^{207}Pb—^{13}C COUPLING CONSTANTS^{b} OF [2-(DIMETHYLAMINOMETHYL)PHENYL]$_n$LEAD (n = 2, 4)^{c}

n	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(CH_2)	C(CH_3)
2	216.9 (1158)	148.6 (10)	127.5^{d} (38)	123.8 (—)^{e}	126.4^{d} (39)	136.2 (22)	69.5 (25)	45.1 (28)
4	159.5 (723)	144.2 (65)	130.7 (98)	129.3 (24)	128.4 (114)	136.3 (85)	65.8 (44)	45.7

^{a}In ppm; reference TMS. ^{b}In Hz; in parentheses. ^{c}In $CDCl_3$. ^{d}Tentatively assigned. ^{e}Not observed.

The NMR spectra of the plumbylene have been recorded and compared with those of tetrakis[2-(dimethylaminomethyl)phenyl]lead. It can readily be seen that the ^{1}H chemical shifts of corresponding protons have rather similar values in the two compounds (Table 1). More interesting features are evident in the ^{207}Pb—^{1}H -couplings, both the coupling constants, $^{3}J(^{207}\text{Pb}—^{1}\text{H}(6))$ and $^{4}J(^{207}\text{Pb}—^{1}\text{H}(7))$ being smaller for the diaryllead compound. The ^{13}C NMR data are presented in Table 2. A surprising downfield shift of about 57 ppm relative to the tetraaryllead compound is observed for C(1) of the diaryllead compound, while the coupling ^{207}Pb—^{13}C(1) increases from 723 Hz for the tetraaryllead to 1158 Hz for the diaryllead compound. We assume that an increased *s*-electron density in the lead—carbon bond causes this large value for the latter coupling. On the other hand, the other ^{207}Pb—^{13}C(Ar) coupling constants of the diaryllead compound are smaller than those of the tetraaryllead compound. The presence of a coupling between lead and the carbon atoms of the $N(CH_3)_2$ group in the plumbylene is indicative of an appreciable lead—nitrogen interaction. In contrast, tetrakis[2-(dimethylaminomethyl)phenyl]lead showed no coupling between lead and the $N(CH_3)_2$ carbon atoms. No signal was found in the ESR spectrum, suggesting that the plumbylene possesses no unpaired electrons.

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