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Preliminary communication

A π-carbanion Grignard reagent

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A considerable amount of information concerning the stereochemistry of organomagnesium compounds has been accumulated recently[1]. However, other than X-ray powder diffraction evidence that $(C_5H_5)_2Mg$ is isostructural with $(C_5H_5)_2Fe$[10], no structural data are currently available concerning the coordination of unsaturated organic groups to magnesium. Recently[2], a spectroscopic study of C_5H_5MgBr in solution has indicated that this molecule contains a π-$C_5H_5^-$ anion. We wish to report the confirmation of this configuration for $C_5H_5MgBr{\cdot}(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ in the solid state.

$C_5H_5MgBr{\cdot}(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ was crystallized from C_5H_5MgBr in diethyl ether by the slow addition of $(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$. From Weissenberg and precession photographs, the Laue symmetry was determined to be *mmm* with systematic absences observed for the reflections $(0kl)$, $k+l = 2n+1$ and $(hk0)$, $h = 2n+1$. The latter are consistent with either of the space groups, *Pnma* or $Pn2_1a$. The unit cell parameters as obtained by the least-squares refinement of the $\sin\theta/\lambda$ values of 12 reflections carefully centered on a Picker X-ray diffractometer, are $a = 23.96(5)$, $b = 12.63(4)$, $c = 11.56(5)$ Å, (MoK_α, $t = 22°$), $\rho_c = 1.36$ g/cm^3 for 8 molecules of $C_5H_5MgBr{\cdot}(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ per unit cell. It was not possible to obtain a reliable observed density due to crystal instability. The crystal used for data collection was rectangular in shape with dimensions 0.42 x 0.45 x 0.45 mm. Absorption corrections, but not extinction corrections, were applied to the experimental data. Statistical tests were ambiguous and did not confirm either space group. Attempts to solve the structure in the space group *Pnma* assuming an ordered model were unsuccessful, and the final refinement was made in the space group $Pn2_1a$ with 2 molecules in the asymmetric unit. Full matrix least-squares refinement of 864 observed reflections measured on a Picker four-circle diffractometer has given an *R* factor of 0.083. This model assumed anisotropic refinement on the magnesium and bromine atoms, but isotropic refinement on all nitrogen and carbon atoms. No hydrogen atoms were included. The largest isotropic temperature factor was 9.1. The average configuration of the two $C_5H_5MgBr{\cdot}(C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$ molecules is shown in Fig. 1.

The average Mg–tertiary amine nitrogen distance (2.26 ± 0.09 Å) is comparable

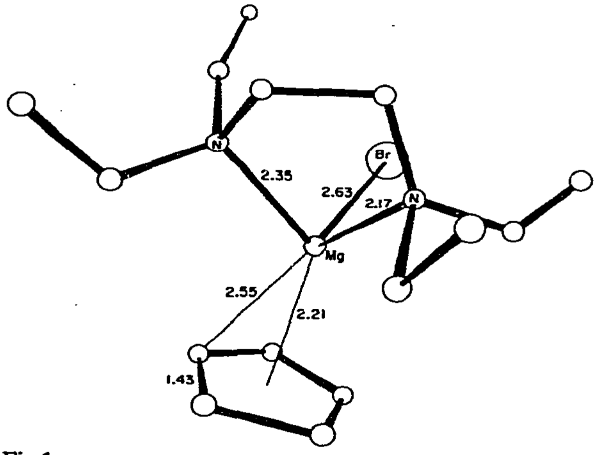

Fig.1.

to that observed in $(CH_3)_2Mg[N(CH_2)_3CH]_2$[3] (2.239(6) Å). The N–Mg–N angle is 82.5 ± 0.5° for the two independent molecules and is about 3° less than what we have observed for the corresponding angle in ethylenediamine lithium compounds. The terminal Mg–Br distance (2.63(1) Å) is the same as that for the six-coordinate magnesium in $MgBr_2(C_4H_8O)_4$[4] but significantly longer than the four-coordinate Mg–Br distance in $C_2H_5MgBr[(C_2H_5)_2O]_2$[5] (2.48(1) Å) or $C_6H_5MgBr[(C_2H_5)_2O]_2$[6] (2.44(1) Å). The average N–Mg–Br angle is 94.9 ± 3.5°. In both molecules in the asymmetric unit, the perpendicular from the Mg atom to the plane of the cyclopentadienyl ring intersects the plane within 0.1 Å of the center of the five-membered ring. The average ring C–C distance of 1.43(3) Å is also consistent with a π-$C_5H_5^-$ group being coordinated to the magnesium atom. The closest approach of the magnesium atom to the plane of the cyclopentadienyl group is 2.21(4) Å with an average Mg–C distance of 2.55 ± 0.05 Å.

It is interesting to compare the magnesium–π-carbon distance with those obtained for other *"pentahapto"* cyclopentadienyl complexes (Table 1). Using the magnesium structure as a reference, we note that the changes in M–π-C distances follow the changes in the atomic radii of the metals themselves, except for the Fe and Co family cyclopentadienyl compounds. This suggests that as far as structural results are concerned, only these families offer any unusual features, with metal–ring carbon distances much shorter than anticipated. This result is consistent with a significant covalent metal–ring bond order in the ferrocene and cobaltocene derivatives. The presence of *d* orbitals in the other transition metals does not significantly alter the structures predicted by an extension of the structural data for C_5H_5MgBr.

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TABLE 1

COMPARISON OF METAL–CARBON ATOM DISTANCES IN METAL CYCLOPENTADIENYL COMPLEXES

Metal	*M–π-C*[a]	*Ref.*	*(Mg–C)-(M–C)*	*Ref.*	Δr[b]
Ti	(2.41)	8	0.14		0.13
V	(2.28), 2.30	9, 10	0.27	9	0.26
Nb	2.45	11	0.10		0.14
Cr	2.25, 2.22	12, 10	0.30	12	0.33
Mo	2.35	13	0.20		0.21
W	2.36	14	0.19		0.21
Mn	2.17	15	0.38		0.34
Re	2.28	16	0.27		0.23
Fe	2.04	21	0.51		0.34
Ru	2.26, 2.21	18, 19	0.34	19	0.26
Co	(2.07), 2.13	20, 10	0.48	20	0.35
Rh	2.24	21	0.31		0.26
Ni	2.20, 2.20	22, 10	0.35	14	0.36
Pd	2.26	23	0.29		0.23
Mg	2.55				

[a] Values in parentheses are calculated from the relation $[r(\text{M–ring})]^2 + 1.21^2 = [r(\text{M–}\pi\text{-C})]^2$ where 1.21 Å = distance from π-C to the center of the ring if $r(\text{C–C}) = 1.43$ Å. The average metal–carbon distances are used. [b] $\Delta r = r(\text{Mg}) - r(\text{M})$ where r_i = metallic radii with ligancy = 12 as given by ref. 7.

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