

Synthesis and Structure of Bis(indenyl)magnesium

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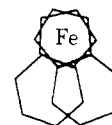
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Abstract: Bis(indenyl)magnesium has been prepared by the thermal decomposition of indenylmagnesium bromide. $\text{Mg}(\text{C}_9\text{H}_7)_2$ crystallizes in the orthorhombic space group $P2_12_1$ with cell dimensions $a = 21.497$ (8), $b = 12.378$ (5), and $c = 10.396$ (5) Å, and $\rho_{\text{calcd}} = 1.22$ g/cm³ for $Z = 8$. Least-squares refinement of three-dimensional X-ray data measured by counter methods gave a conventional R factor of 0.066 for 1112 unique observed reflections. The structure exhibits magnesium atoms in two different environments: one is bonded to the five-membered portion of an indenyl ring in a pentahapto fashion and to two others through essentially only one carbon atom; the second magnesium atom is coordinated to one ring in a pentahapto fashion and to two others through two carbon atoms. Thus there are both bridge and terminal indenyl groups. The closest bridging carbon–magnesium atom approach is 2.26 (1) Å, only slightly longer than a normal σ -bond length. The average pentahapto ring carbon–magnesium atom distance is 2.43 Å. The relation of structure to bonding in $\text{Fe}(\text{C}_5\text{H}_5)_2$, $\text{Mg}(\text{C}_5\text{H}_5)_2$, $\text{Fe}(\text{C}_9\text{H}_7)_2$, and $\text{Mg}(\text{C}_9\text{H}_7)_2$ is discussed.

The properties of bis(cyclopentadienyl)magnesium have been the subject of a great many investigations since its initial preparation¹ in 1954. As an intermediate in the production of other cyclopentadienyl compounds, the substance offers certain advantages over the commonly used alkali metal counterparts. $\text{Mg}(\text{C}_5\text{H}_5)_2$ may be quite readily prepared² in quantitative yield from the high temperature reaction of cyclopentadiene with magnesium metal and purified by sublimation. Its high solubility in hydrocarbon solvents also affords a wider range of synthetic prospects.

The relation of $\text{Mg}(\text{C}_5\text{H}_5)_2$ to the bis(cyclopentadienyl) derivatives of the transition metals has proved to be a point of some controversy.^{3,4} Although compounds of the type $\text{M}(\text{C}_5\text{H}_5)_2$ ($\text{M} = \text{Mg}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) are all isostructural,^{5–7} early magnetic, spectral, and chemical investigations led to the conclusion that the bonding in the magnesium and manganese compounds is essentially ionic.^{3,8} Subsequent studies of the vibrational spectra of bis(cyclopentadienyl)magnesium indicated, however, the presence of covalent ring-to-metal bonding which is weaker than that in ferrocene.⁴

Compared to the role of the cyclopentadienyl group in the renaissance of organometallic chemistry, the part played by the indenyl moiety has been small indeed. Very few indenyl transition metal complexes have been reported,^{9–11} and bis(indenyl)magnesium has been noteworthy in its absence. Bis(indenyl)iron exists in the solid state as a sandwich compound which exhibits the gauche configuration¹²



Based on the geometrical analogy between $\text{Fe}(\text{C}_5\text{H}_5)_2$ and $\text{Mg}(\text{C}_5\text{H}_5)_2$, one might expect $\text{Mg}(\text{C}_9\text{H}_7)_2$ to be similar in structure to $\text{Fe}(\text{C}_9\text{H}_7)_2$. Such is not the case. We wish to report the preparation and crystal structure of bis(indenyl)magnesium, and to discuss the relation of the new compound to the well-known bis(cyclopentadienyl)magnesium.

Experimental Section

Bis(indenyl)magnesium was prepared by the thermal decomposition (190°) of indenylmagnesium bromide under vacuum ($\sim 10^{-4}$ mm). The white crystalline air-sensitive substance was separated from an accompanying yellow oil and purified by sublimation. The net yield of pure product was 25%. Single crystals of $\text{Mg}(\text{C}_9\text{H}_7)_2$ were also grown by sublimation and sealed in thin-walled glass capillaries. Preliminary unit cell parameters were determined by precession ($\text{Cu K}\alpha$) photographs. Final lattice parameters as determined from a least-squares refinement of $(\sin \theta/\lambda)^2$ values for 12 reflections accurately centered on a diffractometer are given in Table I.

Table I. Crystal Data

Mol formula:	$\text{Mg}(\text{C}_9\text{H}_7)_2$
Mol wt:	254.6
Linear abs coeff μ :	9.30 cm ⁻¹
Calcd density:	1.22 g/cm ³
Max crystal dimensions:	0.10 × 0.14 × 0.55 mm
Space group:	orthorhombic, $P2_12_1$
Molecules/unit cell:	8
Cell constants: ^a	$a = 21.497$ (8), $b = 12.378$ (5), $c = 10.396$ (5) Å
Cell vol:	2766 Å ³

^a $\text{Cu K}\alpha$ radiation, λ 1.54051 Å. Ambient temperature of 24°.

Data were taken on an ENRAF-NONIUS CAD-4 diffractometer with graphite crystal monochromated copper radiation. The crystal was aligned on the diffractometer such that the rod axis was coincident with the ϕ axis of the diffractometer. The diffracted intensities were collected by the ω - 2θ scan technique with a takeoff angle of 3.5°. The scan rate was variable and was determined by a fast (20° min⁻¹) prescan. Calculated speeds based on the net in-

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Table II. Final Fractional Coordinates and Anisotropic Thermal Parameters^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mg(1)	0.4238 (1)	0.8469 (2)	0.5414 (3)	36 (1)	58 (3)	95 (4)	-4 (2)	5 (2)	-6 (3)
Mg(2)	0.3932 (1)	0.6182 (2)	0.9413 (3)	24 (1)	59 (3)	123 (5)	0 (2)	5 (2)	8 (3)
C(1)	0.3551 (7)	0.8116 (11)	0.3567 (15)	62 (7)	86 (14)	199 (27)	34 (9)	-40 (11)	-9 (16)
C(2)	0.4085 (11)	0.8671 (9)	0.3223 (13)	131 (13)	38 (10)	148 (21)	-22 (10)	12 (15)	-26 (14)
C(3)	0.4608 (8)	0.8071 (11)	0.3342 (13)	84 (9)	79 (14)	155 (22)	-54 (9)	47 (12)	-49 (17)
C(4)	0.4415 (6)	0.7041 (10)	0.3829 (11)	41 (5)	101 (14)	112 (17)	2 (7)	7 (8)	-45 (13)
C(5)	0.4745 (6)	0.6071 (13)	0.4155 (15)	47 (6)	158 (19)	231 (29)	24 (10)	1 (10)	-47 (22)
C(6)	0.4404 (11)	0.5188 (11)	0.4631 (19)	124 (15)	58 (15)	238 (33)	29 (14)	11 (25)	-9 (20)
C(7)	0.3761 (12)	0.5252 (14)	0.4701 (18)	142 (18)	103 (21)	192 (33)	-63 (19)	-16 (25)	-49 (23)
C(8)	0.3446 (6)	0.6125 (13)	0.4372 (16)	47 (6)	175 (20)	205 (26)	-54 (11)	-14 (11)	-41 (23)
C(9)	0.3769 (5)	0.7058 (10)	0.3933 (11)	33 (5)	110 (14)	124 (17)	-23 (6)	-5 (7)	-37 (13)
C(10)	0.3946 (9)	0.7352 (11)	0.7029 (11)	96 (10)	112 (14)	75 (16)	-60 (10)	21 (9)	-18 (12)
C(11)	0.4436 (8)	0.7285 (10)	0.7825 (18)	82 (9)	57 (10)	267 (31)	-5 (8)	86 (13)	7 (16)
C(12)	0.4390 (6)	0.7922 (12)	0.8847 (15)	27 (5)	167 (19)	291 (31)	-35 (8)	-39 (10)	163 (21)
C(13)	0.3836 (5)	0.8450 (8)	0.8806 (10)	26 (4)	55 (9)	131 (15)	-14 (5)	-1 (7)	7 (10)
C(14)	0.5240 (8)	0.9263 (11)	0.9697 (17)	83 (9)	81 (16)	268 (35)	-31 (10)	66 (18)	-2 (20)
C(15)	0.2914 (9)	0.9553 (10)	0.9257 (18)	99 (9)	79 (12)	222 (28)	19 (8)	102 (15)	15 (16)
C(16)	0.2724 (9)	0.9192 (12)	0.8138 (21)	97 (10)	102 (16)	358 (38)	48 (10)	140 (18)	96 (22)
C(17)	0.2948 (7)	0.8480 (13)	0.7316 (16)	45 (6)	149 (19)	278 (33)	-32 (9)	-36 (12)	132 (22)
C(18)	0.3535 (5)	0.8176 (9)	0.7700 (13)	27 (4)	75 (11)	178 (21)	-23 (6)	-22 (7)	66 (13)
C(19)	0.4774 (4)	0.5403 (8)	1.0483 (11)	21 (4)	82 (10)	135 (17)	14 (5)	8 (7)	-6 (13)
C(20)	0.4685 (4)	0.4682 (8)	0.9443 (12)	25 (3)	56 (8)	172 (17)	1 (4)	7 (8)	27 (12)
C(21)	0.5172 (4)	0.4767 (8)	0.8537 (10)	22 (3)	51 (8)	126 (15)	7 (5)	2 (7)	-4 (10)
C(22)	0.5609 (4)	0.5567 (7)	0.9062 (9)	18 (3)	66 (9)	78 (13)	10 (4)	7 (5)	9 (9)
C(23)	0.6154 (5)	0.5960 (8)	0.8592 (10)	32 (4)	62 (9)	104 (13)	1 (5)	9 (6)	0 (10)
C(24)	0.6485 (5)	0.6677 (9)	0.9327 (14)	35 (5)	91 (12)	172 (21)	-3 (6)	7 (9)	15 (15)
C(25)	0.6243 (5)	0.7062 (7)	1.0513 (14)	26 (4)	53 (9)	206 (23)	-4 (5)	-17 (9)	-15 (13)
C(26)	0.5684 (5)	0.6721 (8)	1.0959 (9)	30 (4)	88 (11)	95 (14)	10 (6)	-17 (7)	-9 (11)
C(27)	0.5347 (4)	0.5930 (7)	1.0258 (10)	13 (3)	73 (9)	107 (14)	10 (4)	8 (5)	10 (11)
C(28)	0.3052 (6)	0.5900 (8)	1.0840 (12)	44 (5)	56 (9)	151 (19)	6 (5)	20 (8)	-6 (12)
C(29)	0.2898 (4)	0.6387 (8)	0.9691 (14)	24 (3)	64 (10)	223 (23)	0 (6)	24 (8)	30 (14)
C(30)	0.2948 (5)	0.5696 (9)	0.8638 (12)	37 (4)	75 (9)	140 (16)	5 (5)	-20 (7)	47 (10)
C(31)	0.3117 (5)	0.4692 (8)	0.9175 (11)	26 (4)	73 (11)	116 (19)	-7 (5)	-3 (7)	-16 (11)
C(32)	0.3228 (5)	0.3640 (12)	0.8573 (12)	36 (4)	151 (15)	126 (16)	-24 (7)	-2 (7)	-30 (15)
C(33)	0.3378 (6)	0.2805 (9)	0.9385 (18)	44 (5)	60 (10)	270 (30)	-3 (6)	1 (11)	-19 (16)
C(34)	0.3448 (6)	0.2926 (9)	1.0700 (15)	46 (5)	76 (12)	202 (24)	-6 (6)	15 (10)	36 (15)
C(35)	0.3373 (5)	0.3909 (9)	1.1307 (11)	39 (4)	89 (11)	130 (16)	-6 (6)	8 (7)	8 (11)
C(36)	0.3187 (4)	0.4806 (9)	1.0511 (11)	19 (3)	107 (13)	91 (15)	-3 (5)	3 (6)	26 (12)

^a Anisotropic thermal parameters $\times 10^4$ defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

intensity gathered in the prescan ranged from 7 to 0.7° min⁻¹. Background counts were collected for 25% of the total scan time at each end of the scan range. For each intensity the scan width was determined by the equation

$$\text{scan range} = A + B \tan \theta$$

where $A = 1.0^\circ$ and $B = 0.45^\circ$. Aperture settings were determined in a like manner with $A = 4$ mm and $B = 4$ mm. The crystal-to-source and crystal-to-detector distances were 21.6 and 20.8 cm, respectively. The lower level and upper level discriminators of the pulse height analyzer were set to obtain a 95% window centered on the Cu K α peak. As a check on the stability of the diffractometer and the crystal, two reflections, the (112) and (410), were measured at 30-min intervals during data collection. No significant variation in the reference intensities was noted.

The standard deviations of the intensities were estimated in the fashion previously described¹³ with the value of the parameter p set at 0.02. Two symmetry related octants were measured out to $2\theta = 120^\circ$; a total of 1112 unique observed reflections ($I > 3\sigma(I)$) were obtained after averaging. The intensities were corrected for Lorentz and polarization effects but not for absorption since the minimum and maximum transmission factors differ by less than 5%.

Fourier calculations were made with the ALFF¹⁴ program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.¹⁵ The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction or anomalous

dispersion. Neutral atom scattering factors were taken from the compilations of Cromer and Waber¹⁶ for Mg and C; those for hydrogen were from "International Tables for X-ray Crystallography."¹⁷ Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE¹⁸ program. Crystal structure illustrations were obtained with the program ORTEP.¹⁹

Solution and Refinement of the Structure. Preliminary density calculations indicated the presence of eight molecules of Mg(C₉H₇)₂ in the unit cell. This was interpreted to mean that there must be two independent molecules in the asymmetric unit, since the space group $P2_12_12_1$ has only fourfold general positions. The interpretation of a sharpened Patterson map, although quite ambiguous, led to the correct placement of both magnesium atoms. Fourier and difference Fourier maps phased on the two magnesium atom positions led to a correct partial model, and subsequent Fourier calculations, preceded by isotropic least-squares refinement of the magnesium and carbon atom positions, allowed the location of all 38 nonhydrogen atoms in the asymmetric unit. Anisotropic refinement with unit weights led to agreement indices of

$$R_1 = \sum(|F_o| - |F_c|) / \sum|F_o| = 0.088$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.092$$

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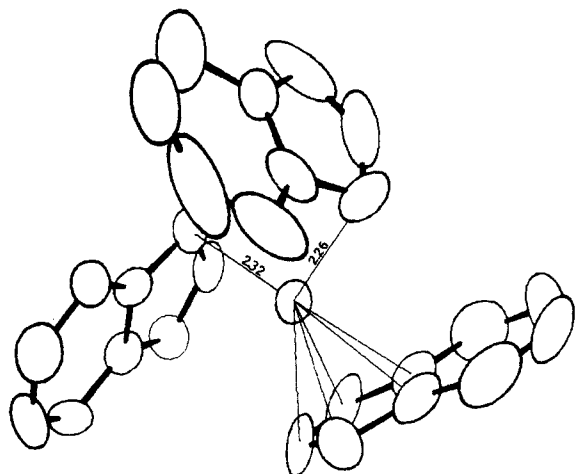


Figure 1. Coordination environment of Mg(1) with the atoms displayed as the 50% probability ellipsoids for thermal motion.

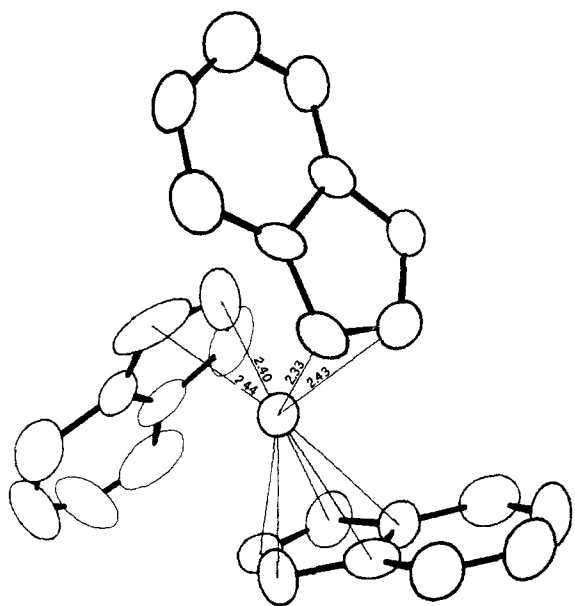


Figure 2. Coordination environment of Mg(2) with the atoms displayed as the 50% probability ellipsoids for thermal motion.

Inclusion of the hydrogen atom contributions at calculated positions and the use of a weighting scheme²⁰ based on the satisfaction of the criterion that $w(|F_o| - |F_c|)^2$ not vary with either F_o or $(\sin \theta)/\lambda$ produced final values of $R_1 = 0.066$ and $R_2 = 0.069$. Unobserved reflections were not included. The largest parameter shifts in the final cycle of refinement were less than 0.20 of their estimated standard deviations. A final difference Fourier map showed no feature greater than $0.4 \text{ e}/\text{\AA}^3$. The standard deviation of an observation of unit weight was 1.04. The final values of the positional and thermal parameters are given in Table II.²¹

Discussion

Bis(indenyl)magnesium in the solid state exhibits magnesium atoms in two different environments and indenyl groups of a fundamentally different nature. As shown in Figures 1, 2, and 3, each magnesium atom is coordinated to three indenyl moieties, one in a penta-hapto fashion and two in a less symmetric manner. The substance exists therefore in an infinite polymeric

(20) The weighting scheme is based on essentially unit weights except for a diminished contribution from the very intense reflections.

(21) See paragraph at end of paper regarding supplementary material.

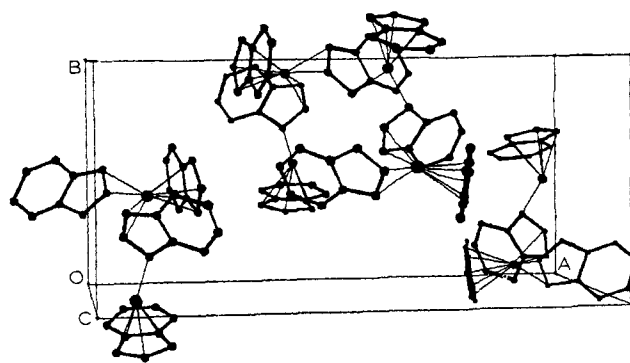


Figure 3. Cell packing of eight $\text{Mg}(\text{C}_9\text{H}_7)_3$ units.

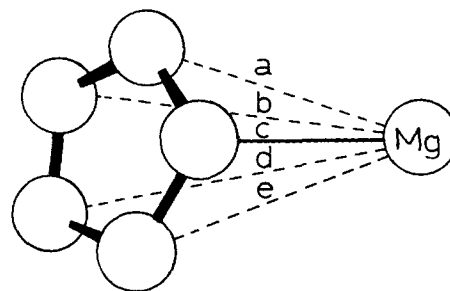


Figure 4. Association of Mg(1) with the five-membered ring fragments of the bridging indenyl groups: $a = 2.93, 2.76 \text{ \AA}$; $b = 3.65, 3.33 \text{ \AA}$; $c = 2.26, 2.32 \text{ \AA}$; $d = 3.63, 3.25 \text{ \AA}$; $e = 2.84, 2.67 \text{ \AA}$.

arrangement with both bridge and terminal indenyl groups, similar to the arrangement of the cyclopentadienyl groups in $\text{Sc}(\text{C}_5\text{H}_5)_3$.¹³

Table III presents the bond length calculations upon

Table III. Magnesium–Carbon Distances (\AA)

Terminal Rings			
Mg(1)–C(1)	2.46 (1)	Mg(2)–C(28)	2.43 (1)
Mg(1)–C(2)	2.31 (1)	Mg(2)–C(29)	2.26 (1)
Mg(1)–C(3)	2.35 (1)	Mg(2)–C(30)	2.34 (1)
Mg(1)–C(4)	2.45 (1)	Mg(2)–C(31)	2.56 (1)
Mg(1)–C(9)	2.54 (1)	Mg(2)–C(36)	2.60 (1)
Bridging Rings			
Mg(1)–C(10)	2.26 (1)	Mg(2)–C(10)	2.87 (1)
Mg(1)–C(11)	2.93 (1)	Mg(2)–C(11)	2.40 (1)
Mg(1)–C(12)	3.65 (1)	Mg(2)–C(12)	2.44 (1)
Mg(1)–C(13)	3.63 (1)	Mg(2)–C(13)	2.88 (1)
Mg(1)–C(18)	2.84 (1)	Mg(2)–C(18)	3.16 (1)
Mg(1)–C(19) ^a	3.33 (1)	Mg(2)–C(19)	2.33 (1)
Mg(1)–C(20) [']	2.76 (1)	Mg(2)–C(20)	2.43 (1)
Mg(1)–C(21) [']	2.32 (1)	Mg(2)–C(21)	3.32 (1)
Mg(1)–C(22) [']	2.67 (1)	Mg(2)–C(22)	3.70 (1)
Mg(1)–C(27) [']	3.25 (1)	Mg(2)–C(27)	3.18 (1)

^a C' related to C by $(\bar{x}, 1/2 + y, 1/2 - z)$ followed by unit cell translations in x and z .

which a detailed description of the structure can be based. The terminal group is bonded to Mg(1) at distances ranging from 2.31 (1) to 2.54 (1) \AA with the longer values corresponding to the sterically less favorable C(4) and C(9) positions. The association with the two bridging ring systems appears to be through essentially only one carbon atom in each group: C(10) at 2.26 (1) \AA and C(21) at 2.32 (1) \AA . The extent to which the interaction is localized with these two atoms is seen with reference to the other distances in the five-membered ring fragments (Figure 4). Thus, in

both cases distances a and e differ by 0.09 Å, and b and d by 0.02 and 0.08 Å. Also the closest approach by another atom from either ring is 2.67 (1) Å, greater than any approach for the pentahapto group.

The second independent magnesium atom, Mg(2), is bonded to its terminal group in a more distorted fashion than is Mg(1); the lengths range from 2.26 (1) to 2.60 (1) Å, but again the long distances correspond to the sterically less favorable C(31) and C(36) positions. In this situation the bridging groups are coordinated through two carbon atoms (2.33 (1) to 2.46 (1) Å).

Quite a number of organomagnesium crystal structures have been done, and a perusal of the compounds and Mg–C lengths given in Table IV shows that they

Table IV. Comparison of Magnesium–Carbon Atom Distances

Compound	Distance	Ref
$C_5H_5MgBr \cdot 2O(C_2H_5)_2$	2.2	<i>a</i>
$C_2H_5MgBr \cdot 2O(C_2H_5)_2$	2.15 (2)	<i>b</i>
$[C_2H_5MgBr \cdot N(C_2H_5)_3]_2$	2.18	<i>c</i>
$[C_2H_5Mg_2Cl_3(C_4H_8O)]_2$	2.19	<i>d</i>
$(CH_3)_2Mg \cdot 2NC_7H_{11}$	2.163 (9)	<i>e</i>
	2.224 (8)	
$[(CH_3)_2N(CH_2)_2NCH_4MgCH_3]_2$	2.104 (4)	<i>f</i>
	2.100 (4)	
$[(CH_3)_2Mg]_\infty$	2.24 (3)	<i>g</i>
$[(C_2H_5)_2Mg]_\infty$	2.26	<i>h</i>
$Mg[Al(CH_3)_4]_2$	2.21 (1)	<i>i</i>
$C_5H_5MgBr \cdot (C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$	2.55 (5)	21

^a G. Stucky and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 4825 (1964). ^b L. J. Guggenberger and R. E. Rundle, *J. Amer. Chem. Soc.*, **90**, 5375 (1968). ^c J. Toney and G. D. Stucky, *Chem. Commun.*, 1168 (1967). ^d J. Toney and G. D. Stucky, *J. Organometal. Chem.*, **28**, 5 (1971). ^e J. Toney and G. D. Stucky, *J. Organometal. Chem.*, **22**, 241 (1970). ^f V. R. Magnuson and G. D. Stucky, *Inorg. Chem.*, **8**, 1427 (1969). ^g E. Weiss, *J. Organometal. Chem.*, **2**, 314 (1964). ^h E. Weiss, *J. Organometal. Chem.*, **4**, 101 (1965). ⁱ J. L. Atwood and G. D. Stucky, *J. Amer. Chem. Soc.*, **91**, 2538 (1969).

may be broken down into three basic types: normal Mg–C σ bonds (2.16 Å), electron-deficient bridge bonds (2.22 Å), and π -bonded derivatives (2.55 Å). Bis(indenyl)magnesium exhibits a range of distances which fall within these extremes. The short ones, 2.26 (1) Å, are quite close to the σ -bond lengths, while the longer ones are near the 2.55 (5) Å standard²² set with $C_5H_5MgBr \cdot (C_2H_5)_2N(CH_2)_2N(C_2H_5)_2$. For the two rings showing essentially pentahapto coordination, the average Mg–C distances are 2.42 and 2.44 Å, significantly less than the 2.55 (5) Å determination. It should be pointed out that Stucky, *et al.*,²² in a comparison of metal–carbon distances in metal cyclopentadienyl complexes found by using 2.55 Å as the Mg–C distance for reference that the only cases where the metal–carbon distances were lower than expected were with $(C_5H_5)_2Fe$ (0.17 Å lower) and $(C_5H_5)_2Co$ (0.13 Å lower). We now find that the assumption of a Mg–C length of 2.43 Å places ferrocene only 0.05 Å shorter and cobaltocene 0.01 Å shorter than predicted. Or, phrasing it differently, the biscyclopentadienyl derivatives of iron and cobalt and bis(indenyl)magnesium all show closer metal–carbon approaches than predicted.²²

As stated previously, $Fe(C_5H_5)_2$ and $Mg(C_5H_5)_2$ are isostructural,^{6,7} but such is not the case for $Fe(C_9H_7)_2$

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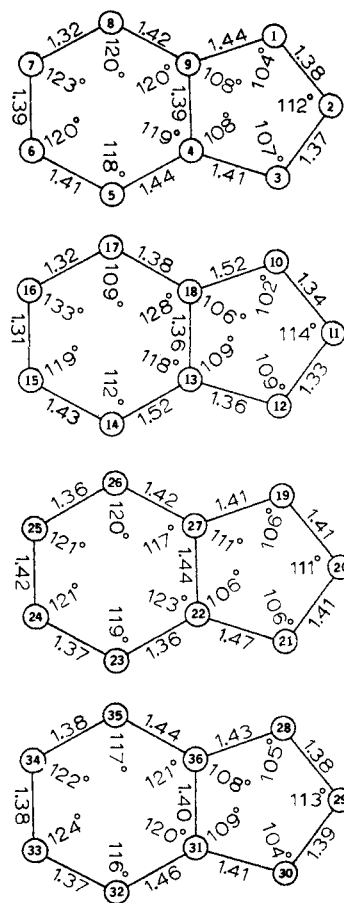


Figure 5. Bond distances and angles within the indenyl groups for $Mg(C_9H_7)_2$.

and $Mg(C_9H_7)_2$. The probable reason for this may be found in the fundamental difference in the ability of the iron and magnesium atoms to bond to a cyclopentadienyl fragment. With the cyclopentadienyl group itself, the bonding mode is not so important in determining the structure, since the covalent model for ferrocene predicts the same geometry as an ionic model. However, the more bulky indenyl group can doubtless pack in a more efficient manner than the sandwich structure allows, and in the absence of strong orbital overlap does so. Therefore, bis(indenyl)iron possesses the essential ferrocene geometry, while bis(indenyl)magnesium does not. That is to say, whether the bonding mode of the magnesium atom is almost totally ionic³ or weak but largely covalent, lattice packing forces determine the gross crystal structure. The degree of orbital overlap evidenced by the preferential magnesium–carbon interactions in some cases is apparently enough to cause a slight orientation of indenyl groups.

The indenyl systems are all planar to within 0.04 Å, and any distortion in either bond distances or angles (Figure 5) may probably be attributed to packing effects. The average bond length values within the five-membered (1.41 Å) and six-membered (1.39 Å) portions agree well with those found in $Sm(C_9H_7)_3$ ²³ and $U(C_9H_7)_3Cl$.²⁴

Bis(indenyl)magnesium has already found some use

(23) J. L. Atwood, J. H. Burns, and P. G. Laubereau, *J. Amer. Chem. Soc.*, **95**, 1830 (1973).

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as a synthetic intermediate in the production of indenyl-lanthanide and -actinide complexes. It has appreciable solubility in aromatic hydrocarbons; $\text{Sm}(\text{C}_9\text{H}_7)_3$,²³ $\text{U}(\text{C}_9\text{H}_7)_3\text{Cl}$,²⁵ and $\text{Sc}(\text{C}_9\text{H}_7)_3$ ²⁶ were all initially prepared from toluene solutions of $\text{Mg}(\text{C}_9\text{H}_7)_2$ mixed with the anhydrous metal chloride.

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American Chemical Society, for financial support of this work.

Supplementary Material Available. Calculated hydrogen atom coordinates, best planes results, and the structure factor table will appear, at the request of the Editor, following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St. N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-994.

The Nature of the Lowest Excited State in Tricarbonylchloro-1,10-phenanthroline-rhenium(I) and Related Complexes

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Abstract: Complexes of the general formula $\text{ClRe}(\text{CO})_3\text{X}$ ($\text{X} = 1,10\text{-phenanthroline}$ and related ligands) are found to undergo radiative decay from their lowest electronically excited state both in 298°K fluid solution and at 77°K in glassy media. Emission lifetimes are near 10^{-5} sec at 77°K in EPA and at least 1 order of magnitude shorter at 298°K in deoxygenated solutions. Luminescence quantum yields at 77°K are of the order of 10^{-1} . Variations in the lowest absorption maximum with X and solvent polarity are consistent with a $\text{M} \rightarrow \text{X} \pi^*$ charge-transfer (CT) transition. The sensitivity of the emission spectrum to its environment and X point to an association with the $\text{M} \rightarrow \text{X} \pi^*$ CT absorption. Both the emission lifetimes and preliminary energy transfer experiments are consistent with an emitting state which has substantial triplet character. The room temperature fluid solution luminescence observed in these complexes constitutes the first direct observation of excited state decay in metal carbonyls under conditions where photochemistry is normally performed. These complexes also exhibit a unique effect referred to as *luminescence rigidochromism* (spectral distribution of luminescence in fluid media and rigid media is vastly different). In these $\text{ClRe}(\text{CO})_3\text{X}$ complexes emission maxima shift up to $\sim 1500 \text{ cm}^{-1}$ depending on the environmental rigidity, yielding red-orange luminescence in fluid solution and yellow-green luminescence in rigid media.

Excited-state decay processes in metal carbonyl complexes are dominated by ligand dissociation in fluid solution.¹ These processes or internal conversion to electronic states inaccessible by direct absorption must occur very rapidly ($\sim 10^{10} \text{ sec}^{-1}$) since no luminescence has been noted for these compounds in solution even though radiative decay rate constants are estimated to be quite large due to high oscillator strengths for observed electronic absorptions.^{1,2} To date no one has claimed direct observation, by any technique, of an electronically excited metal carbonyl in fluid solution at room temperature. Indeed, characterization of the electronically excited states of most metal complexes has been by elucidation of excited-state chemistry³ or by absorption spectroscopy.

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The only metal carbonyl complexes known to luminescence at all are low-spin d^6 W, Mo, Cr substituted carbonyl complexes which emit only at low temperatures.⁴ The $\text{W}(\text{CO})_5\text{L}$ luminescence was assigned to the ${}^3\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1) \rightarrow {}^1\text{A}_1(\text{e}^4\text{b}_2^2)$ ligand field (LF) transition.^{4a} Experiments both in rigid media at 77°K and fluid solution at 298°K showed that the $\sim 3 \times 10^{-6}$ sec excited-state lifetime at 77°K shortens to at least 2×10^{-11} sec at 298°K in solution for $\text{W}(\text{CO})_5(\text{py})$ (py = pyridine). The change in lifetime was attributed to rapid pyridine photodissociation in the 298°K solutions. Some coordination compounds do undergo radiative decay in fluid solution and these include several Cr(III) complexes which give LF luminescence⁶ and Ru(II) or Ir(III) tris-1,10-phenanthroline or tris-2,2'-bipyridine complexes which exhibit spin-

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