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1,4-Dimethyl-2,3-diphenylfulvene: A convenient precursor to heteroatom-substituted-1-methyl-2,5-dimethyl-3,4-diphenylcyclopentadienyl transition metal complexes [1,2]

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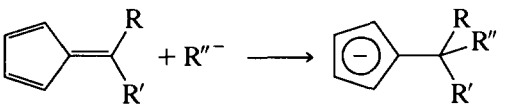
Abstract

Reaction of 2,5-dimethyl-3,4-diphenylcyclopent-2-enone (**1**) with $Ph_3P{=}CH_2$ in THF gave 2,5-dimethyl-3,4-diphenylcyclopent-2-ene-1-ylidene (**2**) in 75% yield. Treatment of **2** with one equivalent of Br_2, followed by two equivalents of triethylamine gave 1,4-dimethyl-2,3-diphenylfulvene (**3**) in 60% overall yield. Treatment of **3** with $LiCH_3$ and LiC_6H_5 followed by $FeCl_2$ gave $[\eta^5\text{-}1\text{-}CH_3CH_2\text{-}2,5\text{-}(CH_3)_2\text{-}3,4\text{-}(C_6H_5)_2C_5]_2Fe$ and $[\eta^5\text{-}1\text{-}C_6H_5CH_2\text{-}2,5\text{-}(CH_3)_2\text{-}3,4\text{-}(C_6H_5)_2C_5]_2Fe$, respectively, in good yield. Treatment of **3** with $LiNHC(CH_3)_3$ and $LiP(C_6H_5)_2$ followed by $FeCl_2$ gave $[\eta^5\text{-}1\text{-}(CH_3)_3CNHCH_2\text{-}2,5\text{-}(CH_3)_2\text{-}3,4\text{-}(C_6H_5)_2C_5]_2Fe$ and $[\eta^5\text{-}1\text{-}(C_6H_5)_2PCH_2\text{-}2,5\text{-}(CH_3)_2\text{-}3,4\text{-}(C_6H_5)_2C_5]_2Fe$, respectively, in good yield. Treatment of **3** with (R)-$LiNHCH(CH_3)C_6H_5$ followed by $FeCl_2$ gave the corresponding enantiomerically pure ferrocene complex (R,R)-$[\eta^5\text{-}1\text{-}C_6H_5CH(CH_3)NHCH_2\text{-}2,5\text{-}(CH_3)_2\text{-}3,4\text{-}(C_6H_5)_2C_5]_2Fe$ in 44% yield.

Keywords: Lithium; Iron; Fulvenes; Metallocenes; Cyclopentadienyl; Chiral

1. Introduction

In recent years there has been considerable interest in the synthesis of organometallic complexes with cyclopentadienyl ligands incorporating amine or phosphine groups [2]. The addition of nucleophiles to fulvenes has proven to be a successful route for the preparation of substituted cyclopentadienyl ligands for use in organometallic chemistry as illustrated below [2a,e,3]. However, the scope of this reaction has been limited because the reaction of substituted fulvenes with heteroatom-based nucleophiles results, in many cases, in deprotonation rather than nucleophilic addition [2k,4]. We have shown previously that this problem can be circumvented by using the much less acidic 1,2,3,4,6-pentamethylfulvene [5]. An alternative approach is to prepare and utilize 1,2,3,4-tetramethylfulvene which contains no competing acidic protons [2a,6]. While 1,2,3,4,6-pentamethylfulvene is prochiral and leads to diastereomers upon the addition of chiral nucleophiles, 1,2,3,4-tetramethylfulvene is not prochiral, thus the addition of chiral nucleophiles does not lead to diastereomers.



$R = CH_3, C_6H_5$

$R' = H, CH_3, C_6H_5$

$R'' = H, CH_3, C_6H_5, CH_2p(C_6H_5)_2$

For several years our group has been developing routes to highly substituted fulvenes for use in organometallic chemistry [1,5,6]. However, we have found these methods to be limited in scope [7]. We therefore found it necessary to develop an alternative synthesis of highly substituted fulvenes.

2. Results and discussion

The preparation of 1,4-dimethyl-2,3-diphenylfulvene (**3**) is shown in Scheme 1. Treatment of 2,5-dimethyl-

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[1] Dedicated to Professor Marvin D. Rausch, with best wishes on the occasion of his 65th birthday.

[2] A preliminary account of this work has appeared, see Ref. [1].

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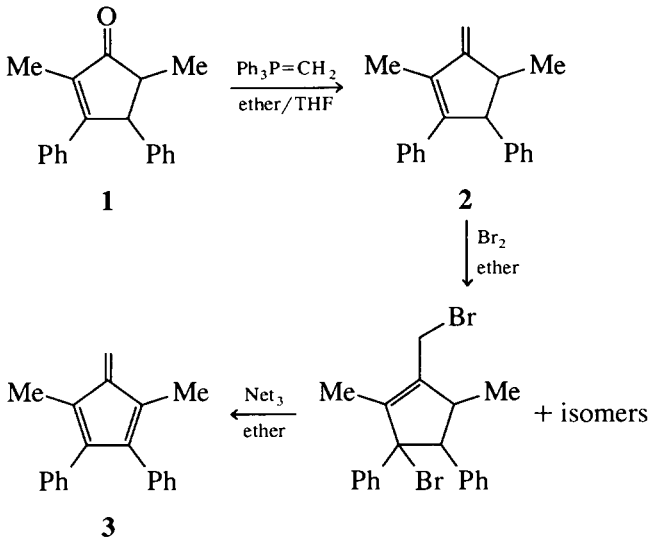
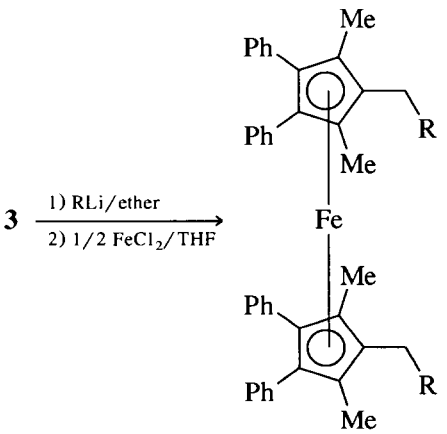


Scheme 1.

3,4-diphenylcyclopent-2-enone (**1**) [8] with $Ph_3P{=}CH_2$ in THF gave 2,5-dimethyl-3,4-diphenylcyclopent-2-ene-1-ylidene (**2**) in 75% yield. Treatment of **2** with one equivalent of Br_2, in ether leads to a mixture of unstable dibromides [9] which were not isolated. Dehydrohalogenation of this mixture with two equivalents of triethylamine gave **3** in 60% overall yield. The ^1H NMR spectrum of **3** was found to be solvent dependent, with the fulvene=CH_2 group shifting from 5.76 δ in $CDCl_3$ to 5.56 δ in C_6D_6.

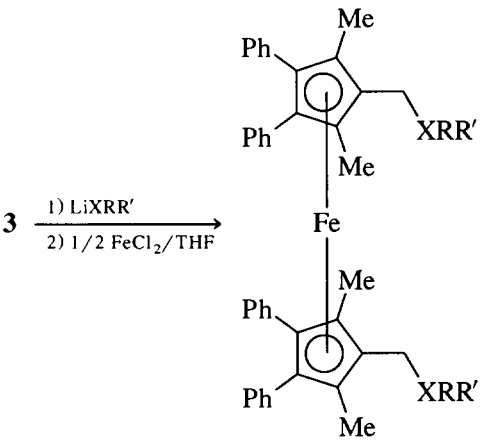
Addition of methyl lithium and phenyl lithium to **3** in ether followed by treatment with $FeCl_2$ in THF gave 1,1'-diethyl-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene (**4**) and 1,1'-dibenzyl-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene (**5**), in 58 and 43% yield respectively.



4 R = CH_3

5 R = C_6H_5

Treatment of **3** with lithium t-butylamide in ether followed by $FeCl_2$ in THF gave 1,1'-bis-t-butylaminomethyl-2-2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene (**6**) in 66% yield. In an analogous manner treatment of **3** with lithium (R)-α-methylbenzylamide followed by $FeCl_2$ lead to enantiomerically pure (R,R)-1,1'-bis(methylbenzylaminomethyl)-2,2',5,5'-dimethyl-3,3',4,4'-diphenylferrocene (**7**) in 44% yield.



6 X = N; R = H; R=$C(CH_3)_2$

7 X = N; R = H; R' = (R)-$CH(CH_3)C_6H_5$

8 X = P; R = R' = C_6H_5

Treatment of **3** with lithium diphenylphosphide [10] in THF followed by the addition of $FeCl_2$ gave 1,1'-bis(diphenylphosphinomethyl)-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene (**8**) in 46% yield.

1,4-Dimethyl-2,3-diphenylfulvene has proven to be a convenient starting material for the preparation of 1,1'-disubstituted-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene derivatives in moderate yield. Further work is in progress to explore the utility of **3** as a starting material for preparation of new enantiomerically pure ligands. In addition, work is in progress to explore the chelating properties of these new ligands.

3. Experimental section

All operations were performed under an atmosphere of dry nitrogen. Solvents were purified by distillation from Na/K alloy under nitrogen. 2,5-Dimethyl-3,4-diphenylcyclopent-2-enone (**1**) [8] and $LiP(C_6H_5)_2$ [10] were prepared by literature methods. Methyl lithium (Aldrich), n-butyl lithium (Aldrich), phenyl lithium (Aldrich), chlorodiphenylphosphine (Aldrich), methyltriphenylphosphtizrhfonium bromide (Aldrich), ferrous chloride (Strem) were used as purchased. (R)-(+)-α-Methylbenzylamine (Aldrich) was dried over 4A molecular sieves, t-butylamine (Aldrich) and triethylamine (Aldrich) were distilled from BaO prior to use. Column chromatography was carried out using silica-gel (Fisher) or neutral alumina (Fisher) under nitrogen.

^1H, and ^{13}C spectra were recorded at 250, and 62.8 MHz, respectively, on a Bruker WM250 NMR spec-

trometer. Spectra were measured at ambient temperature in C_6D_6 or $CDCl_3$ utilizing residual solvent peaks or tetramethylsilane as an internal standard. Melting points were determined on a Mel-Temp apparatus from Laboratory Devices in sealed tubes under nitrogen and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Nocrorss Ga.

3.1. Preparation of 2,5-dimethyl-3,4-diphenylcyclopent-2-ene-1-ylidene (2)

$[Ph_3PCH_3]Br$ 0.68 g (1.9 mmol) was added slowly to a solution of MeLi, 1.3 ml of 1.5 M (1.9 mmol) in ether, and 20 ml of dry THF in a 100 ml three neck flask. The reaction mixture was stirred for 4 h at room temperature. 2,5-Dimethyl-3,4-diphenylcyclopent-2-enone (**1**), 0.49 g (1.9 mmol), was then added dropwise. The reaction mixture was heated under reflux for 48 h, allowed to cool to room temperature and the resulting precipitate filtered and washed with 10 ml of ether. The ether and THF solutions were combined and the solvent removed under vacuum. The residue was dissolved in ether and washed with water until neutral, dried over $MgSO_4$, filtered and the solvent removed under vacuum. The residue was purified by column chromatography on silica-gel (hexane as eluent) to give, upon removal of the solvent under vacuum, 0.37 g (75% yield) of **2** as a white crystalline solid (m.p. 68–69°C).

^{1}H-NMR ($CDCl_3$, TMS) δ 1.71 (d, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.57 (q, 1H, C*H*CH_3), 3.7 (s, 1H, C*H*Ph), 4.71 (s, 1H, CH_2 olefinic), 4.88 (s, 1H, CH_2 olefinic), 6.89–7.18 (m, 10H, Ar); $^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS) δ 11.7 (CH*C*H_3), 20.2 (=C*C*H_3), 47.6 (*C*HCH_3), 61.6 (*C*HPh), 101.0 (=CH_2), 126.1 (p-Ph), 126.7 (p-Ph), [127.7, 127.9, 128.4, 128.6] (o and m-Ph), 128.8 (CH_3C=), 137.1 (i-Ph), 137.4 (i-Ph), 146.0 (=CPh), 160.9 (CH_2=*C*).

IR 3091, 3065, 3039, 3012, 2960, 2933, 2874, 1637, 1611, 1499, 1082, 1037, 871 cm^{-1}.

Anal. Calc. for $C_{20}H_{20}$ C, 92.26; H, 7.74; Found: C, 92.06; H, 7.84.

3.2. Preparation of 1,4-dimethyl-2,3-diphenylfulvene (3)

Compound **2**, 0.73 g (2.8 mmol), was dissolved in 20 ml of ether and cooled to −40°C. Bromine 0.15 ml (2.8 mmol) was added dropwise in the dark and stirring continued at −40°C for 30 min to give an orange solution. The solution was allowed to warm to room temperature and 0.78 ml (5.6 mmol) of freshly distilled Et_3N was added. The solution was stirred for 1 h at room temperature, filtered and washed with three 30 ml portions of water. The water layers were combined and back extracted with ether. The combined ether layers were washed with 30 ml of water dried over $MgSO_4$, filtered and the solvent removed under vacuum, to give 0.57 g (80% yield) of **3** as a red crystalline solid (m.p. 82–83°C).

^{1}H NMR ($CDCl_3$/TMS) δ 2.00 (s, 6H, CH_3), 5.76 (s, 2H, CH_2), 6.88 (m, 4H, Ar), 7.10 (m, 6H, Ar) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, TMS) δ 10.3 (CH_3), 115.4 (=CH_2) 125.3 (p-Ph), 127.7 (m-Ph), 129.5 (o-Ph), 135.9 (=*C*CH_3), 135.8 (=*C*Ph), 142.9 (i-Ar), 154.87 (CH_2=*C*).

IR 3085, 3058, 3039, 2920, 2861, 1604, 1499, 1446, 1077, 919.

Anal. Calc. for $C_{20}H_{18}$ C, 92.92; H, 7.02. Found C, 92.73; H, 7.11.

3.3. Preparation of 1,1'-diethyl,-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene (4)

Methyl lithium, 2.3 ml of 1.5 M (3.5 mmol), in ether was added to 0.92 g (3.5 mmol) of **3** in 10 ml of dry ether at room temperature in a 100 ml three neck flask. The reaction mixture was allowed to stir for 1 h and then the solvent was removed under vacuum. Anhydrous $FeCl_2$ (0.23 g, 1.8 mmol) and 20 ml of dry THF were added and the mixture was refluxed for 2 h. The solution was then cooled to room temperature and the solvent removed under vacuum to give a red-orange oil. This oil was taken up in ether and washed with saturated aqueous ammonium chloride. The organic layer was then dried over $MgSO_4$, filtered and the solvent was removed under vacuum to give 0.84 g of a red oil. The resulting red oil was taken up in a minimum volume of hot methanol, and the solution was allowed to slowly cool to room temperature, and then cooled to 0°C to give 0.61 g (58%) of **4** as an orange crystalline solid (m.p. 62–63°C).

^{1}H NMR (C_6D_6, TMS) δ 0.96 (t, 6H, CH_3), 1.98 (s, 12H, CH_3), 2.37 (q, 4H, CH_2), 6.95–7.33 (m, 20H, Ar); $^{13}C\{^1H\}$ NMR (C_6D_6, TMS) δ 10.9 (CH_3), 14.3 (*C*H_3CH_2), 18.7 (CH_3CH_2), 79.4 (CH_3Cp), 86.5 (CH_3CH_2Cp), 87.3 (Ph*C*p), 125.6 (o-Ph), 127.0 (m-Ph), 131.6 (p-Ph), 136.8 (i-Ph).

Anal. Calc. for $C_{42}H_{42}Fe$ C, 83.71; H, 7.02. Found C, 84.08; H, 7.09.

3.4. Preparation of 1,1'-dibenzyl-2,2'5,5'-tetramethyl-3,3'4,4'-tetraphenylferrocene (5)

Phenyl lithium, 2.1 ml of 1.8 M (3.8 mmol), in ether was added to 1.0 g (3.8 mmol) of 1,4-dimethyl-2,3-diphenylfulvene in 15 ml of dry ether in a 100 ml three neck flask. The mixture was stirred under reflux for 2.5 h. The solution was allowed to cool to room temperature and the solvent was removed under vacuum. Anhydrous $FeCl_2$ (0.24 g, 1.9 mmol) and 20 ml of dry THF were added and the reaction mixture was refluxed for 2 h. The solution was cooled to room temperature and the solvent removed under vacuum. The residue was puri-

fied by chromatography on neutral alumina using 1:9 benzene:hexane as eluant to give a red band which upon removal of the solvent under vacuum gave 0.59 g (43%) of **5** as an orange-red crystalline solid (m.p. 79–80°C).

^{1}H-NMR-(C_6D_6, TMS) δ 1.96 (s, 12H, CH_3), 3.89 (s, 4H, CH_2), 6.95–7.35 (m, 30H, Ar); $^{13}C\{^1H\}$-NMR (C_6D_6, TMS) δ 11.5 (CH_3), 31.5 (CH_2), 80.6 (CH_3Cp), 84.6 ($PhCH_2Cp$), 87.0 (PhCp), [125.8, 127.2, 128.1, 128.4, 131.6] (Ph), 136.4 (i-Ph), 140.5 (i-Ph).

IR (CCl_4), 3092, 3039, 2920, 1617, 1499, 1459, 1084, 1031.

Anal Calc. for $C_{52}H_{46}Fe$: C, 85.94, H, 6.38; Found: C, 86.44, H, 6.74.

3.5. Preparation of 1,1'-bis-t-butylaminomethyl-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenyl-ferrocene (6)

n-BuLi 1.3 ml of 1.6M (2 mmol), in hexane was added to 0.2 ml (2 mmol) of t-butylamine in 10 ml of dry ether at 0°C, and stirred for 45 minutes in a 50 ml three neck flask. To this resulting white suspension 0.5 g (2 mmol) of **3** was added and the solution was refluxed for 2.5 h. The reaction mixture was cooled to 0°C and 0.13 g (1 mmol) of anhydrous $FeCl_2$ added, and the solution refluxed for 3 h. The reaction mixture was allowed to cool to room temperature, filtered, and the solvent removed under vacuum. The residue was dissolved in a small volume of ether, cooled to −10°C and filtered. The solvent was removed under vacuum to give 0.47 g (66%) of **6** as an orange solid (m.p. 75–80°C, dec).

^{1}H-NMR (C_6D_6, TMS) δ 1.06 (s, 18H, CH_3), 2.12 (s, 12H, CH_3), 3.66 (s, 4H, CH_2), 6.99–7.41 (m, 20H Ar); $^{13}C\{^1H\}$-NMR (C_6D_6, TMS) δ 11.2 (CH_3Cp), 28.7 ($(CH_3)_3C$), 38.6 (CH_2), 50.23 ($(CH_3)_3C$), 81.0 (CH_3Cp), 83.8 (CH_2Cp), 87.0 (PhCp), 125.8 (p-Ph), 127.1 (o-Ph), 131.6 (m-Ph), 136.5 (i-Ph).

IR(KBr) 3322, 3058, 2967, 2914, 2868, 1604, 1505, 1479, 1446, 1235, 1025, 650.

Anal Calc. for $C_{48}H_{56}N_2Fe$: C, 80.43; H, 7.87; N, 3.91. Found C, 81.07; H, 8.01, N 3.30.

3.6. Preparation of (R,R)-1,1'-bis-methylbenzyl-aminomethyl-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenyl-ferrocene (7)

CH_3Li, 1.4 ml of 1.5 M (2.1 mmol), in ether was added to 0.27 ml (2.1 mmol) of (R)-(+)-α-methylbenzylamine in 20 ml of dry ether at 0°C in a 50 ml three neck flask. The solution was stirred for 30 min. at 0°C. A solution of 0.50 g (2.1 mmol) of **3** was added dropwise to the solution at room temperature and stirred for 2 h. Anhydrous $FeCl_2$ 0.13 g (1.05 mmol) was added to the solution at 0°C, the reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was filtered and the solvent removed under vacuum. The residue was dissolved in a small volume of ether, cooled to −10°C and then filtered. The solvent was removed under vacuum to give an orange oil. The oil was dissolved in ether and the solution filtered through neutral alumina. The solvent was removed under vacuum to give 0.37 g (44%) of (**7**) as an orange solid (m.p. 55–60°C dec).

^{1}H-NMR (C_6D_6, TMS) 0.90 (m, 2H, NH), 1.24 (d, 6H, CH_3), 1.95 (s, 6H, CH_3), 1.98 (s, 6H, CH_3), 3.55 (s, 4H, CH_2), 3.67 (m, 2H, CH), 6.94–7.37 (m, 30H, Ar). $^{13}C\{^1H\}$-NMR (C_6D_6, TMS) δ 11.1, (CH_3Cp), 11.2 (CH_3Cp), 24.3 (CH_3N), 43.8 (CH_2), 58.9 (CH), 80.9 (CH_3Cp), 83.4 (CH_2Cp), 86.8 (PhCp), 87.0 (PhCp), 125.7 (p-Ph), [126.7, 126.8, 127.1, 127.1, 128.2, 128.2, 129.6, 131.5] (Ph), 136.1 (i-Ph), 136.2 (i-Ph).

IR(KBr) 3322, 3091, 3033, 2973, 2914, 2868, 1604, 1512, 1492, 1453, 1117, 1077, 958, 551.

Anal. Calc. for $C_{56}H_{56}N_2Fe$: C, 82.74, H, 6.94. Found C, 82.46; H 7.02.

3.7. Preparation of 1,1'-bis-diphenylphosphinomethyl-2,2',5,5'-tetramethyl-3,3',4,4'-tetraphenylferrocene (8)

Lithium diphenylphosphide [10], prepared from 0.34 ml (1.9 mmol) of chlorophenylphosphine and 0.06 g (8.0 mmol) of lithium in 10 ml of dry THF, was added to 0.5 g (1.9 mmol) of **3** in a 100 ml three neck flask. The resulting reaction mixture was stirred overnight at room temperature and then refluxed for 1 h. The reaction mixture was allowed to cool to room temperature, 0.12 g (0.95 mmol) of anhydrous $FeCl_2$ was added and the reaction mixture refluxed for 5 h. The solution was allowed to cool to room temperature, filtered and the solvent removed under vacuum. The resulting residue was purified by chromatography on neutral alumina using 1:1 benzene:hexane to give a red band which upon removal of the solvent under vacuum gave 0.41 g (45.8% yield) of **8** as an orange solid (m.p. 222–223°C).

^{1}H-NMR (C_6D_6, TMS) δ 1.75 (s, 12H, CH_3), 3.21 (s, 4H, CH_2), 7.11–7.49 (m, 40H, Ar); $^{13}C\{^1H\}$-NMR (C_6D_6,TMS) δ 11.7 (CH_3), 26.4 (d, J_{C-P} = 18.8, CH_2), 80.4 (CH_3Cp), 81.9 (d, J_{C-P} = 14.8 Hz, CH_2Cp), 87.1 (PhCp), 125.7 (p-Ph), 127.6 (Ph), 128.0 (d, J_{C-P} = 11.7, Ph), 128.3 (d, J_{C-P} = 9.9, Ph), 131.5 (Ph), 133.2 (d, J_{C-P} = 19.4), 136.6 (i-Ph), 138.6 (i-Ph) (d, J_{C-P} = 17.2).

IR 3065, 2960, 2920, 2854, 1604, 1558, 1512, 1439, 1262, 1104, 1025.

Anal. Calc. for $C_{64}H_{56}P_2Fe$: C, 81,52, H, 5.98. Found C, 81.37, H 6.05.

Acknowledgements

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