The Reaction of Cyclooctatetraene with $[RuCl(H)(PPh_3)_3]$†

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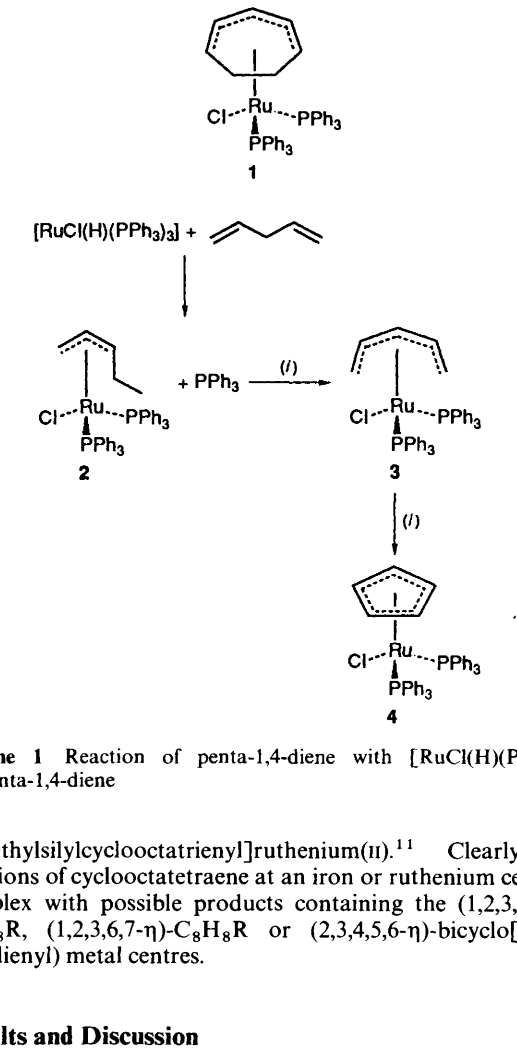
It has been shown that $[RuCl(H)(PPh_3)_3]$ reacts with cyclooctatetraene to give three isomers, which are characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy to be two isomers of $[Ru(\eta^5\text{-}C_8H_9)Cl(PPh_3)_2]$ and {(2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl}chlorobis(triphenylphosphine)ruthenium(II). The interconversion of the two isomers of the (1,2,3,4,5-η)-C_8H_9 derivative and the generation of an apparent plane of symmetry by exchange in the bicyclo[5.1.0]octadienyl derivative has been investigated quantitatively.

The reaction of dienes and trienes with $[RuCl(H)(PPh_3)_3]$ have been studied in order to investigate the mechanism of addition of this very active hydrogenation catalyst to unsaturated molecules.[1] The product is stabilised by co-ordination of the double bonds to the ruthenium. Thus when $[RuCl(H)(PPh_3)_3]$ is treated with cycloheptatriene $[Ru(\eta^5\text{-}C_7H_9)Cl(PPh_3)_2]$ **1** is quantitatively formed.[2] When penta-1,4-diene is used $[Ru(\eta^3\text{-}1\text{-}anti\text{-}EtC_3H_4)Cl(PPh_3)_2]$ **2** is initially formed, but this reacts with more penta-1,4-diene to give $[Ru(\eta^5\text{-}C_5H_7)Cl(PPh_3)_2]$ **3** and then $[Ru(\eta^5\text{-}C_5H_5)Cl(PPh_3)_2]$ **4**, see Scheme 1.[3]

In the present work the reaction of $[RuCl(H)(PPh_3)_3]$ with cyclooctatetraene is examined. There have been a number of studies of the reactions of cyclooctatetraene when co-ordinated to iron or ruthenium. The principal reaction has been the protonation of cyclooctatetraene. The protonation of $[Ru(\eta^4\text{-}C_8H_8)(CO)_3]$ yields {(2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl}tricarbonylruthenium(1+), which then isomerises to either the (1,2,3,4,7-η)- or (1,2,3,6,7-η)-C_8H_9 derivative.[4] Similarly, protonation of $[Ru(\eta^4\text{-}C_8H_8)(CO)_2(PPh_3)]$ yields the (1,2,3,6,7-η)-C_8H_9 monocation.[4,5] The analogous iron compound $[Fe(\eta^4\text{-}C_8H_8)(CO)_3]$ is protonated to give the (1,2,3,4,5-η)-C_8H_9 monocation as the initial product, which then isomerises to {(2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl}tricarbonyliron(1+).[6] If hydrogen chloride is used as the acid, then protonation of $[M(\eta^4\text{-}C_8H_8)(CO)_3]$ (M = Fe or Ru) yields the tricarbonylchloro[(1,2,3-η)-cyclooctatrienyl]metal compounds.[7] Protonation of $[Ru(\eta^4\text{-}C_8H_8)(\eta^6\text{-arene})]$ (arene = 1,3,5-$Me_3C_6H_3$, C_6Me_6 or $C_6H_5Bu^t$ yields initially the (1,2,3,4,5-η)-C_8H_9 monocations which in the cases of arene = 1,3,5-$Me_3C_6H_3$ or C_6Me_6, isomerises to the (1,2,3,6,7-η)-C_8H_9 monocations.[8] The reaction is not restricted to the addition of H^+ to the cyclooctatetraene ring. Recently, $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ (allyl = CH_2CHCH_2 or CH_2CMeCH_2) has been used as a source of $[allyl]^+$ to add to $[Ru(\eta^4\text{-}C_8H_8)(CO)_2L]$ (L = CO or PPh_3) to yield the (1,2,3,6,7-η)-C_8H_9 monocations and to $[Fe(\eta^4\text{-}C_8H_8)(CO)_2(CNBu^t)]$ to yield a mixture of the (1,2,3,4,5-η)-C_8H_9 monocation and {(2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl}(*tert*-butylisocyanide)dicarbonyliron(1+).[9] Electrochemical oxidation of $[Ru(\eta^4\text{-}C_8H_8)(CO)_2(PPh_3)]$ yields the corresponding dimer containing (1,2,3,6,7-η:1′,2′,3′,6′,7′-η′)-$C_{16}H_{16}$.[5] This reaction contrasts with the dimerisation of $[Fe(\eta^4\text{-}C_8H_8)(CO)_3]$ to yield bis{(2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl}hexacarbonyldiiron(1+).[10] The insertion of cyclooctatetraene into a ruthenium–silicon bond is known in the case of *cis*-$[Ru(SiMe_3)_2(CO)_4]$, where treatment with cyclooctatetraene in refluxing hexane yields dicarbonyl(trimethylsilyl)[(1,2,3,6,7-η)-trimethylsilylcyclooctatrienyl]ruthenium(II).[11] Clearly the reactions of cyclooctatetraene at an iron or ruthenium centre is complex with possible products containing the (1,2,3,4,5-η)-C_8H_8R, (1,2,3,6,7-η)-C_8H_8R or (2,3,4,5,6-η)-bicyclo[5.1.0]-octadienyl) metal centres.



Scheme 1 Reaction of penta-1,4-diene with $[RuCl(H)(PPh_3)_3]$. (*i*) Penta-1,4-diene

Results and Discussion

The complex $[RuCl(H)(PPh_3)_3]$ in CD_2Cl_2 was treated with cyclooctatetraene at −78 °C and then warmed to room temperature, and the subsequent reaction monitored by 162 MHz ^{31}P NMR spectroscopy. The broad signal due to $[RuCl(H)(PPh_3)_3]$ decreased and new broad signals centred around δ 28 appeared. On cooling to −60 °C the ^{31}P NMR signals sharpened and three AX patterns were resolved at δ 33.1 and 25.5, $^2J(^{31}P\text{-}^{31}P)$ = 22 Hz, δ 31.9 and 19.0, $^2J(^{31}P\text{-}^{31}P)$ = 24 Hz and δ 29.4 and 26.9, $^2J(^{31}P\text{-}^{31}P)$ = 26 Hz, in the ratio 0.45 : 0.41 : 1.00 due to isomers **5a**, **5b** and **5c**. The signals are

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† *Non-SI unit employed*: cal = 4.184 J.

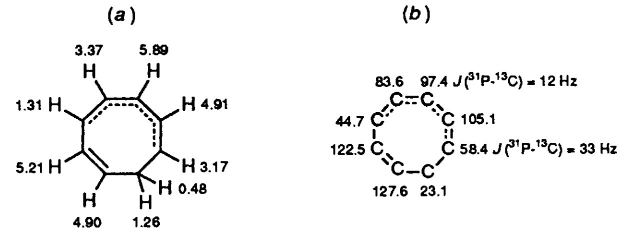


Fig. 1 The ^1H and ^{13}C NMR chemical shifts of the C_8H_9 ligand in isomer **5c**

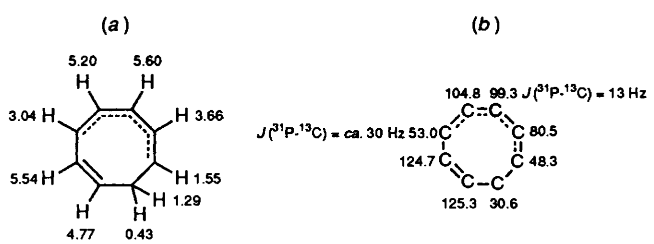
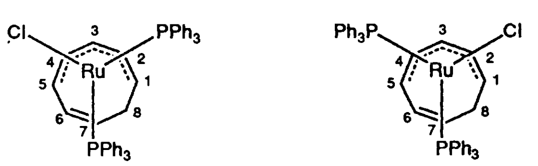
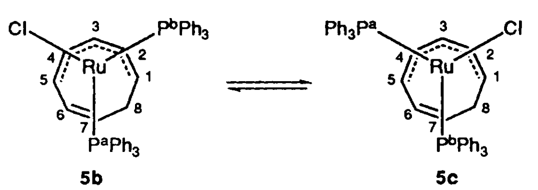


Fig. 2 The ^1H and ^{13}C NMR chemical shifts of the C_8H_9 ligand in isomer **5b**



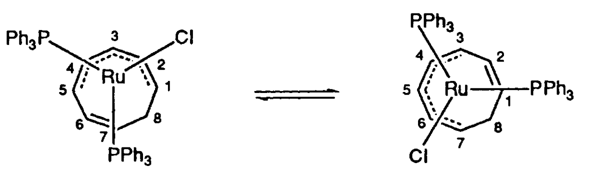
5b **5c**

Fig. 3 The probable structures of isomers **5b** and **5c**



5b **5c**

Scheme 2 The interconversion of isomers **5b** and **5c**



Scheme 3 The interconversion of isomers **5c** and **5c′**

quite temperature dependent with the corresponding shifts at −19.5 °C being δ 32.8 and 26.2, 31.6 and 19.9 and 29.6 and 25.9. On account of the marked temperature dependence of the chemical shift of the low-frequency reference of isomer **5c**, there is overlap with the low-frequency signal due to isomer **5a** at around −30 °C.

Magnetisation transfer was carried out at −19.5 °C, using ^{31}P DANTE measurements. The signals at δ 32.8, 31.6, 29.6 and 19.9 were sequentially inverted. No magnetisation transfer was detected between isomer **5a** and either **5b** or **5c**. Magnetisation transfer was observed between the two inequivalent PPh_3 ligands of isomer **5a**, with a rate of 50 s^{-1}, corresponding to $\Delta G^{\ddagger}_{253.5}$ = 12.8 kcal mol^{-1}, and between all the remaining four PPh_3 signals. If these sites are labelled 1–4 at δ 31.6, 19.9, 29.6 and 25.9, respectively, then due to the symmetry of the system, $k_{13} = k_{24}$ and $k_{14} = k_{23}$. This treatment gave $k_{12} = 0.27$ s^{-1}, $k_{13} = k_{24} = 0.41$ s^{-1}, $k_{14} = k_{23} = 31.11$ s^{-1} and $k_{34} = 3.34$ s^{-1}, with an error of 0.490. When k_{12}, k_{13} and k_{24} were set equal to 0, then $k_{14} = k_{23} = 31.72$ s^{-1} and $k_{34} = 3.80$ s^{-1}, with an error of 0.495. If k_{34} is also set equal to 0, then the error increases to 1.561, showing that this assumption is not justified. It is therefore concluded that k_{14}, k_{23} and k_{34} are significant, corresponding to $\Delta G^{\ddagger}_{253.5}$ = 13.0 kcal mol^{-1} for 1 $\longrightarrow$ 4 and 2 $\longrightarrow$ 3 and 14.1 kcal mol^{-1} for 3 $\longleftrightarrow$ 4. No reliable values can be attached to k_{12}, k_{13} or k_{24} but these rate constants must be small, and an upper value of 1 s^{-1} can be given corresponding to an upper value of $\Delta G^{\ddagger}_{253.5}$ = 14.7 kcal mol^{-1}. Phosphorus-31 magnetisation-transfer measurements were also performed at 0 °C, to examine if there is any significant exchange between **5b**/**5c** and **5a**. None was detected, placing an upper limit of 2 s^{-1} for exchange from **5b**/**5c** to **5a**. Hence the activation energy for the conversion is greater than 15.5 kcal mol^{-1}. In order to explain these data it is necessary to determine the structures of isomers **5a**–**5c**.

The structures were determined by a combination of ^1H and ^{13}C NMR spectroscopy. At −60 °C, decoupling difference ^1H NMR spectroscopy was used to determine the sequence of hydrogen signals around each C_8H_9 ring. For the major isomer, **5c**, the problem was complicated by the accidental degeneracy of two signals at δ 4.91. Decoupling difference established the connectivity permitting the assignment in Fig. 1(*a*). These ^1H nuclei were related to the attached ^{13}C nuclei by a two-dimensional ^{13}C-{^1H} correlation spectrum and the assignments are given in Fig. 1(*b*). These measurements establish that two adjacent carbon nuclei which have chemical shifts in the range expected for sp^2 nuclei at δ 122.5 and 127.6 are attached to the protons at δ 5.21 and 4.90 respectively. This permits the unambiguous positioning of the unco-ordinated carbon atoms within the ring and hence the determination of the structure as the (1,2,3,4,5-η)-C_8H_9 isomer. This is in contrast with dicarbonyl[(1,2,3,6,7-η)-cyclooctatrienyl](trimethylsilyl)-ruthenium(II).[11]

The ^{31}P magnetisation measurements have established chemical exchange between isomers **5c** and **5b**. Hence, qualitative ^1H magnetisation-transfer measurements at −25 °C were used to establish the ^1H–^1H connectivity between **5b** and **5c**. In addition, decoupling difference was used to establish coupling connectivity within **5b**. The ^1H NMR assignments are given in Fig. 2(*a*). These ^1H nuclei were related to the attached ^{13}C nuclei by a two-dimensional ^{13}C-{^1H} correlation spectrum and the assignments are given in Fig. 2(*b*). The position of the unco-ordinated double bond and dienyl moiety are identical to that in **5c**, but the chemical shifts of the dienyl are significantly different. The carbon which shows the large coupling to ^{31}P has moved from one end of the dienyl to the other. By analogy with [Ru(η^5-C_7H_9)Cl(PPh_3)$_2$], it is proposed that the two isomers are as given in Fig. 3. The ^{31}P NMR spectrum of [Ru(η^5-C_7H_9)Cl(PPh_3)$_2$] shows that the PPh_3 groups are inequivalent. The $J(^{31}P-^{13}C)$ coupling to the ^{13}C NMR signals at δ 53.0 and 99.3 for **5b** and δ 58.4 and 97.4 for **5c** is consistent with *trans*-PPh_3 groups. The ^{13}C chemical shifts are also consistent with the relative *trans* influence of the PPh_3 and Cl ligands.

Examination of the ^1H chemical shifts of isomers **5b** and **5c** shows the danger of assigning structures from NMR spectra without a CH correlation measurement. The ^1H NMR spectra are equally consistent with a (1,2,5,6,7-η)-C_8H_9 bonding arrangement. It is only when the connectivity has been established by ^1H decoupling and the ^{13}C NMR signals have been assigned by CH correlation that it is possible unambiguously to assign the structure.

The interconversion of isomers **5b** and **5c** occurs by rotation of the RuCl(PPh_3)$_2$ moiety with respect to the η^5-C_8H_9 ligand, see Scheme 2. This mechanism is established for the analogous [Ru(η^5-C_7H_9)Cl(PPh_3)$_2$] derivative.[2] The mechanism which interconverts the inequivalent PPh_3 ligands in **5c** produces pairwise exchange between the signals at δ 5.89 and 1.31, 4.91 and 5.21, and 4.90 and 3.17. This is consistent with the exchange shown in Scheme 3. Possible intramolecular processes which are consistent with this exchange are either *via* [Ru(η^7-C_8H_9)(PPh_3)$_2$]$^+$ or chloro[(3,4,5-η)-cyclooctatrienyl]bis(triphenylphosphine)ruthenium(II).

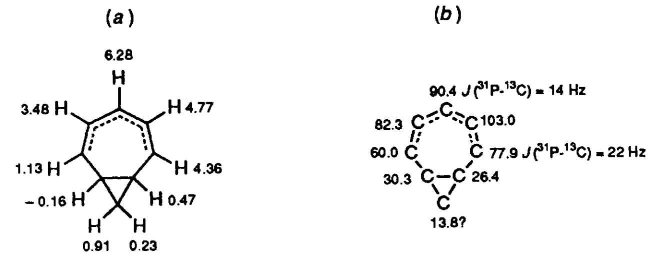


Fig. 4 The ^1H and ^{13}C NMR chemical shifts of the C_8H_9 ligand in isomer **5a**

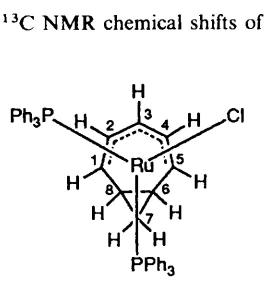


Fig. 5 The probable structure of isomer **5a**

The ^1H NMR spectrum of the third isomer, **5a** was assigned by a combination of decoupling difference and magnetisation-transfer measurements, see Fig. 4(*a*). The dynamic process which causes exchange of the PPh_3 ^{31}P NMR signals causes pairwise exchange across the ring, exchanging the pairs of protons at δ 3.48 and 4.77, 1.13 and 4.36 and −0.16 and 0.47. The ^1H NMR signals were related to the ^{13}C NMR signals by a two-dimensional $^{13}C\text{-}\{^1H\}$ correlation experiment, and this is the basis of the assignments given in Fig. 4(*b*).

The position of the $RuCl(PPh_3)_2$ fragment with respect to the organic bicyclo[5.1.0]octadienyl ligand was deduced from $J(^{31}P\text{-}^{13}C)$, which is large when the PPh_3 is *trans* to the carbon atom. The probable structure of isomer **5a** is given in Fig. 5. The ^{13}C chemical shifts are consistent with the relative *trans* influence of Cl and PPh_3. The exchange of the two inequivalent PPh_3 groups and pairwise proton exchange is consistent with the rotation of the $RuCl(PPh_3)_2$ moiety.

There have been a number of preparations of compounds containing the $\eta^5\text{-}C_8H_9$ ligand involving protonation of the $\eta^4\text{-}C_8H_8$ ligand, yielding a wide selection of products. Many of the published reactions have relied on ^1H NMR data for elucidation of the structure. In the present work it is clear that the structures of **5b** and **5c** could not have been reliably determined by ^1H NMR spectroscopy alone, and so published structures relying purely on such data must be viewed with caution.

In the present work the addition of cyclooctatetraene to $[RuCl(H)(PPh_3)_3]$ yields both $[Ru(\eta^5\text{-}C_8H_9)Cl(PPh_3)_2]$, two isomers, and {(2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl}-chlorobis(triphenylphosphine)ruthenium(II). The ratio of the compounds is approximately constant. As the (1,2,3,4,5-η)-C_8H_9 metal compounds {'metal' = $[Fe(CO)_3]^+$ or $[Ru(\eta^6\text{-}arene)]^+$, arene = 1,3,5-$Me_3C_6H_3$ or C_6Me_6} isomerise to the (1,2,3,6,7-η)-C_8H_9 derivatives it is probable that in the case when 'metal' = $RuCl(PPh_3)_2$ a similar isomerisation occurs. The ratio observed for **5a**:**5b**:**5c** is independent of whether the reaction between cyclooctatetraene and $[RuCl(H)(PPh_3)_3]$ has been stopped before completion, or has been allowed to continue for several hours at room temperature. It is therefore probable that the rate of isomerisation of $[Ru(\eta^5\text{-}C_8H_9)Cl(PPh_3)_2]$ to the (2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl compound is faster than the formation of the former from cyclooctatetraene and $[RuCl(H)(PPh_3)_3]$, and the product ratio reflects an equilibrium between the isomers. At 20 °C the half-life of the reaction between cyclooctatetraene and $[RuCl(H)(PPh_3)_3]$ is only a few minutes, giving an upper limit to the activation energy of the interconversion of the (1,2,3,4,5-η)-C_8H_9 and (2,3,4,5,6-η)-bicyclo[5.1.0]octadienyl derivatives as 21 kcal mol^{-1}. Magnetisation-transfer measurements have established a lower activation energy for this process of 15.5 kcal mol^{-1}. It is clear from this and earlier work that there are only very small energy differences between the co-ordination modes of the $\eta^5\text{-}C_8H_9$ ligand.

Experimental

The NMR spectra in CD_2Cl_2 were measured on a Bruker WH400 spectrometer. The temperatures were measured using a Comark electronic thermometer, by replacing the sample with an NMR tube containing a thermocouple in CH_2Cl_2. Carbon-13 chemical shifts were referenced to the central resonance of CD_2Cl_2 at δ 53.6, ^{31}P chemical shifts were determined relative to external 85% H_3PO_4.

The following experimental procedure was employed to carry out the DANTE[12] measurements. A suitable temperature was chosen so that there was a little line broadening due to exchange. After the spectrometer had stabilised at that temperature, the T_1 values of the $P(OMe)_3$ groups were estimated using the $10D_1\text{–}\pi\text{–}D_1\text{–}\frac{\pi}{2}$ pulse sequence, adjusting the delay, D_1, for null signal. Subsequently the relaxation delay was taken as $10D_1$. The DANTE pulse length was optimised for maximum signal inversion. The measurements were carried out using the pulse sequence: $\{[\text{read free induction decay (f.i.d.)}\text{–}\{10D_1\text{–}(D_2\text{–}P_1)_{30}\text{–}D_3\text{–}\frac{\pi}{2}\text{–acquire}\}_8\text{–write f.i.d.–change } D_3]_m\text{–reset exchange delay, } D_3\}_n$, with m typically 10 and n chosen to give adequate signal:noise ratio. Typical values are D_1 = 3 s, D_2 = 0.2 ms, P_1 = 2.8 μs, D_3 = m values with the minimum being 3 μs and the largest $10D_1$, and $\frac{\pi}{2}$ pulse = 40.0 μs. The remaining times were chosen to give a spread over the exchange and relaxation times, typically: 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2 and 0.4 s. This sequence has the advantage that any temperature drift during the experiment will be spread over all the measurements. The resulting data were analysed as previously described.[13]

The complex $[RuCl(H)(PPh_3)_3]$ was prepared following established procedures.[14] The cyclooctatetraene, purchased from Aldrich, was purified by passage through alumina shortly before use. The NMR solutions were prepared by taking $[RuCl(H)(PPh_3)_3]$ (*ca.* 50 mg) in a Schlenk tube, and adding degassed CD_2Cl_2 (*ca.* 0.3 cm^3). A syringe was used to transfer the solution to a nitrogen-filled 5 mm NMR tube fitted with a B10 socket and subaseal. The tube was immersed in liquid nitrogen. A solution of cyclooctatetraene (50 μl) in degassed CD_2Cl_2 (*ca.* 0.1 cm^3) was added. When the solution had frozen the tube was transferred to a solid CO_2–acetone bath at −78 °C and the contents mixed by shaking. The tube was then brought slowly to room temperature, and the reaction observed as the violet solution of $[RuCl(H)(PPh_3)_3]$ was consumed and the yellow-brown products formed. The tube was then placed in the probe.

Acknowledgements

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