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Journal:	<i>Dalton Transactions</i>
Manuscript ID:	DT-LET-03-2015-001099.R1
Article Type:	Letter
Date Submitted by the Author:	17-Apr-2015
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Carbonyl fluxionality in Rh-containing Transition Metal Carbonyl Clusters (TMCCs) and the Ligand Polyhedral Model (LPM)

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Resume

Experimental results (recent IR, DFT calculations and modern multinuclear NMR measurements on Rh-containing clusters, together with earlier VT multinuclear NMR measurements) show that the use of the **Ligand Polyhedral Model (LPM)** to provide a general mechanism for ligand fluxionality in **Transition Metal Carbonyl Clusters (TMCCs) in solution** cannot be sustained; instead there are numerous examples of only partial CO-migration over either part or sometimes the whole of the Rh-polyhedron as well as rhodium and carbonyl polyhedral rearrangements of Rh₉- and Rh₁₀-TMCCs containing an interstitial P when, in the high temperature limiting spectra, all the metals and all the carbonyls become equivalent and show time-averaged values of ¹J(Rh–P) and ²J(P–CO) respectively.

The sixty year saga (1952-2013) of the solid state structure of Fe₃(CO)₁₂, *viz* Fe₃(CO)₁₀(μ-CO)₂, has recently been summarised by Dahl, one of the authors of the original structural determination.¹ The crystals of Fe₃(CO)₁₂ are disordered and the LPM arose initially in an attempt to rationalise this by considering the packing of the metal polyhedron within the ligand polyhedron in the solid state.² Subsequently, it was extended to provide an explanation of carbonyl fluxionality in solution,³ which is proposed to involve librations and polyhedral rearrangements of the metal/ligand polyhedra, and Johnson⁴ prefers the LPM to explain carbonyl fluxionality rather than the more localised exchanges collated by Mann for tri-nuclear carbonyl clusters;⁵ it is worthwhile noting that in the recent editorial collated by Brian Johnson “In memory of Lord Jack Lewis”, Evans⁶ highlights the NMR studies, carried out with Jack Lewis in Cambridge, on Os₃(CO)₁₀(PEt₃)₂,⁷ which has all terminal COs, and

$^{13}\text{C}/^{31}\text{P}$ NMR show that CO-exchange occurs selectively along one edge of the Os_3 -triangle at low temperatures – this process only involves six of the COs and a mechanism involving a CO-bridged intermediate, $\text{Os}_3(\text{CO})_8(\mu\text{-CO})_2(\text{PET}_3)_2$, is proposed^{6,7} rather than the LPM. For tri-nuclear clusters there are no metals with $I = \frac{1}{2}$ and suitable abundance for NMR studies; it is therefore difficult to be sure of the motion of the ligand polyhedron with respect to the metal polyhedron as there is no unambiguous reference point. King *et al*⁸ has calculated that the C_{2v} -isomer of $\text{Fe}_3(\text{CO})_{10}(\mu\text{-CO})_2$ has a global minimum energy below that of the all-terminal-CO D_{3h} -isomer, which is analogous to the known structures of $\text{Ru}_3(\text{CO})_{12}$ ⁹ and $\text{Os}_3(\text{CO})_{12}$.¹⁰ The energies of both the C_{2v} - and D_{3h} -isomers will be affected by solvation and related DFT calculations¹¹ on $\text{Rh}_4(\text{CO})_{12}$ correctly predicts that the lowest energy structure to be the C_{3v} structure, $\text{Rh}_4(\text{CO})_9(\mu\text{-CO})_3$, found in the solid state,¹² with the Rh_4 -tetrahedron enveloped in a $(\text{CO})_{12}$ -icosahedron. These calculations also show that an all-terminal isomer, related to the structure of $\text{Ir}_4(\text{CO})_{12}$,¹³ is of not much higher energy and IR measurements in hexane¹⁴ show that these two isomers co-exist in solution. IR spectra of the all-terminal isomer show that the COs adopt a C_{3v} -anti-cuboctahedral arrangement rather than the T_d -cuboctahedral arrangement adopted by $\text{Ir}_4(\text{CO})_{12}$,¹⁴ which shows that rearrangement of dodeca-polyhedra in solution is facile, despite suggestions by Johnson that this will be a high energy process.¹⁵

For Rh-containing clusters, it is possible through multinuclear NMR measurements to deduce unambiguously the pathways of ligand migration over the Rh-skeleton since, of all the transition metals, ^{103}Rh is unique and 100% abundant with $I = \frac{1}{2}$. Using modern NMR methods, it is also possible to obtain quantitative information about the energetics of these migrations.^{16,17} Furthermore, phosphine substituted clusters provide a point of reference for these migrations and, if $^1\text{J}(\text{Rh-X})$ ($X = ^{31}\text{P}$) is retained, the metal polyhedron is tethered to the ligand polyhedron, restricting the movement of both the metal and ligand polyhedra. For $[\text{Rh}_6(\text{CO})_{15}\text{L}]$ ($\text{L} = \text{PR}_3$),¹⁶ we have been able to show that there are a number of different migrations occurring with different rates whereas we think that the Johnson LPM paper predicts that exchange of COs is completely described by a single rate constant.¹⁵ It is worth noting that early VT measurements¹⁸ on $[\text{Rh}_4(\text{CO})_8\text{L}_4]$ ($\text{L} = \text{P}(\text{OPh})_3$) showed that at low temperature the NMR spectra are consistent with the solid state structure,¹⁹ which consists of a Rh_4 -tetrahedron within an icosahedral ligand framework with 3 bridging-COs, one L per Rh and the Ls are arranged as far apart as possible. At +82 °C, the COs migrate over all the Rh and each L remains associated with one Rh and are coupled to 3 other Rh, which have all become equivalent. This is consistent with an intermediate which contains all terminal COs

and each $\text{Rh}(\text{CO})_2\text{L}$ -group undergoes rapid rotation about the pseudo- C_3 -axis (see Fig. 1); we think that these simultaneous CO/L-migrations cannot be explained using the LPM and it is easier to visualise this exchange as involving terminal/bridge CO-exchange as used for $\text{Os}_3(\text{CO})_{10}(\text{PEt}_3)_2$ *vide infra*.

Fig. 1 here

Although, it may be argued that the inability of phosphine ligands to form bridge bonds puts them outside the scope of the LPM, we have also established that concerted carbonyl exchange processes involving subsets of the total carbonyl shell are consistent with the VT NMR studies we have reported on a number of homoleptic carbonyl clusters. Over the years, using VT measurements we have shown that there is often only partial CO-migration over part of the Rh-polyhedron eg $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2-}$,²⁰ (pairwise-CO-exchange of 5 terminal with 2 edge-bridging COs around the $(\text{Rh}_B)_4$ -equatorial plane and the terminal COs on each Rh_A and the 4 bridging COs between Rh_A and Rh_B remain unchanged, see Fig. 2),

Fig. 2 here

$[\text{Rh}_7(\text{CO})_{16}]^{3-}$,²¹ (the terminal/edge-bridging COs exchange around the triangular- $(\text{Rh}_C)_3$ -face when other COs remain static, see Fig. 3),

Fig. 3 here

$[\text{Rh}_{13}\text{H}_n(\text{CO})_{24}]^{(5-n)-}$ ($n = 2, 3$),²² (Schematic structure of $[\text{Rh}_{13}\text{H}_n(\text{CO})_{24}]^{(5-n)-}$ ($n = 2$ or 3), see Fig. 4; the arrows show one of the 3 pathways which involve edge/terminal CO-exchange. There is also a second equivalent pathway, which is related to the first by the plane of symmetry, while a third pathway becomes only equivalent after migration *via* the first or second pathway. A fourth pathway which involves only the $(\text{Rh}_B)_6$ -hexagonal plane does not preserve the original distribution of COs and is thus of higher energy and does not occur on the NMR time-scale²²); we feel that **all these CO-migrations cannot arise from localised librations of the metal polyhedron within a CO-polyhedron using the LPM.**

Fig. 4 here

Furthermore, it should be noted that for both the mono-capped square antiprismatic cluster, $[\text{Rh}_9\text{P}(\text{CO})_{21}]^{2-}$, and the bi-capped square antiprismatic cluster, $[\text{Rh}_{10}\text{P}(\text{CO})_{22}]^{3-}$, which both contain an interstitial P, both rhodium and carbonyl polyhedral rearrangements occur; in the high temperature limiting NMR spectra of both clusters, all the metals become equivalent and all the carbonyls become equivalent and show time-averaged values of $^1\text{J}(\text{Rh}-\text{P})$ and $^2\text{J}(\text{P}-\text{CO})$ respectively.²³ Here, the interstitial P provides an unambiguous point of reference and the LPM cannot account for these rearrangements.

Acknowledgements

This research has been supported by St. Petersburg State University (research grant 0.37.169.2014) and Russian Foundation for Basic Research (grant 13-03-12411).

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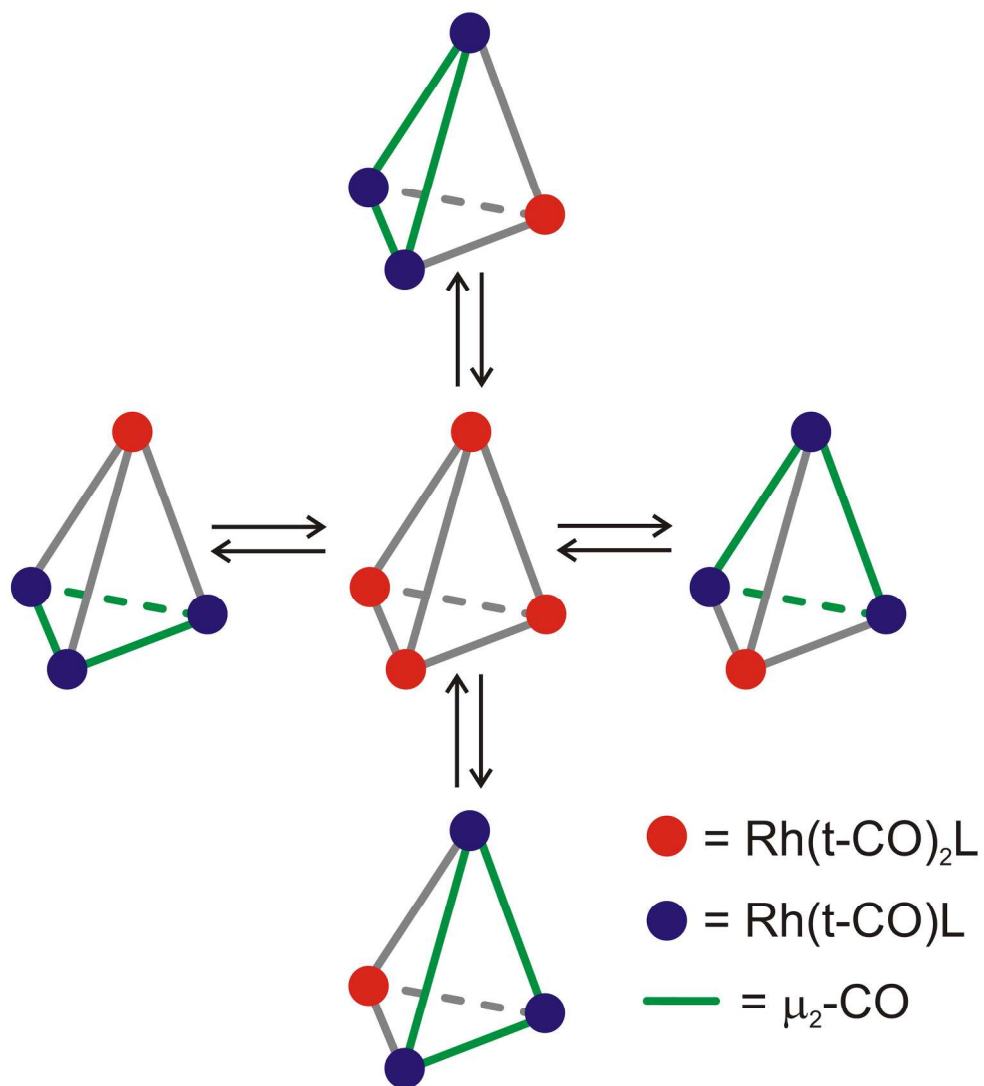
Legends to Figures

Figure 1. Schematic representation of the fluxionality in $\text{Rh}_4(\text{CO})_5(\mu\text{-CO})_3\text{L}_4$ at +82 °C. Rhodium atoms are shown as red or blue balls. Each L is bonded to different Rh and are arranged as far apart as possible; they remain attached to their parent Rh during the exchange process. Red rhodiums are associated with one L and two terminal COs; blue rhodiums are associated with one L, one terminal CO and two edge-bridging COs shown in green. The intermediate state (in the center of the figure) contains only terminal COs.

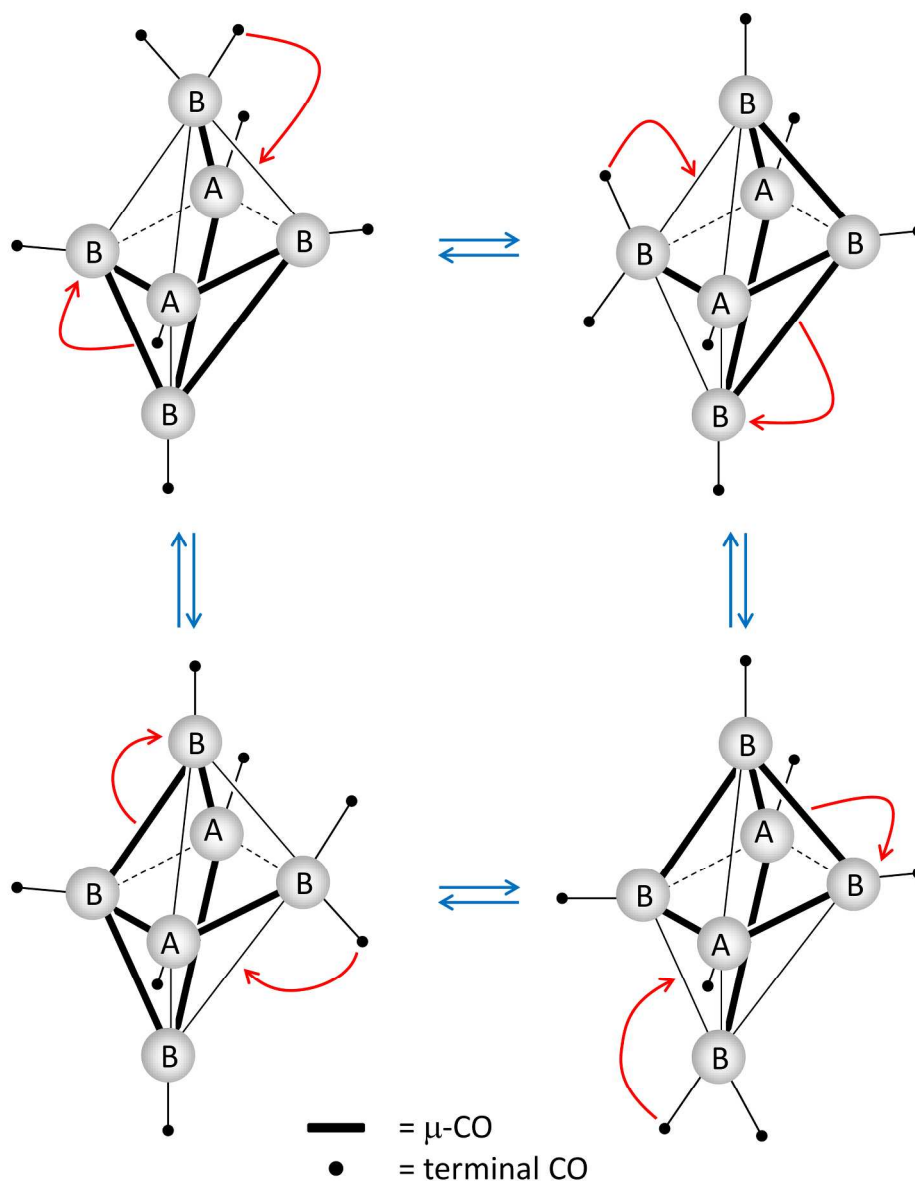
Figure 2. Schematic representation of carbonyl fluxionality in $[\text{Rh}_6\text{C}(\text{CO})_{13}]^{2-}$. Adapted from Ref. 20.

Figure 3. Schematic representation of $[\text{Rh}_7(\text{CO})_{16}]^{3-}$. The exchanging terminal/bridging COs (green and blue) are on the triangular- $\text{Rh}_3(\text{C})$ -face. Adapted from Ref. 21.

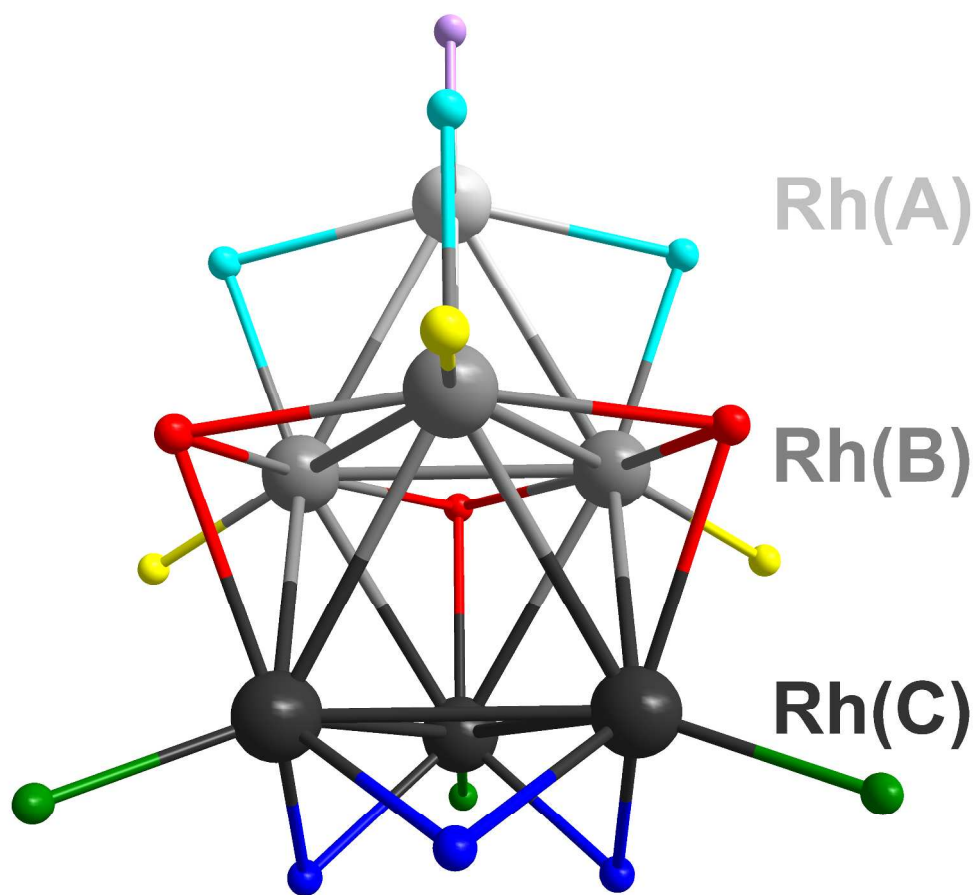
Figure 4. Schematic structure of $[\text{Rh}_{13}\text{H}_n(\text{CO})_{24}]^{(5-n)-}$ ($n = 2$ or 3). The arrows show one of the 3 pathways which involve edge/terminal CO-exchange. See text. Adapted from Ref. 22.



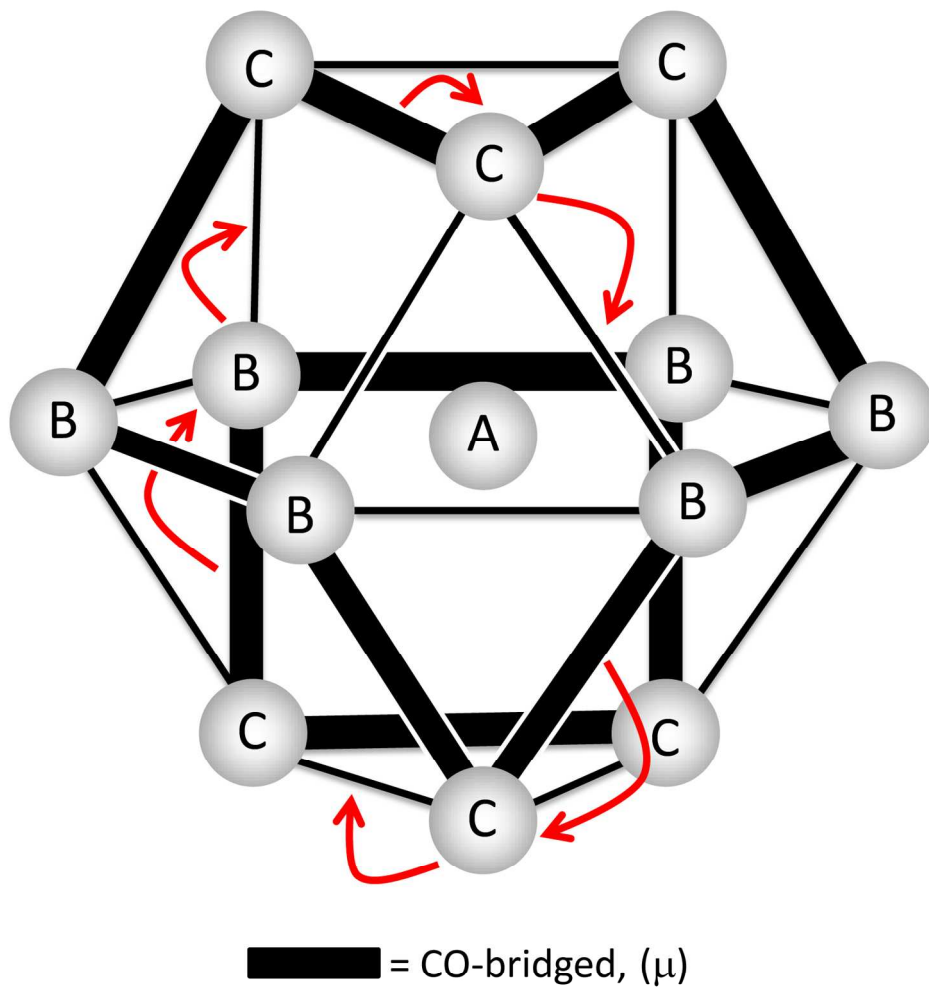
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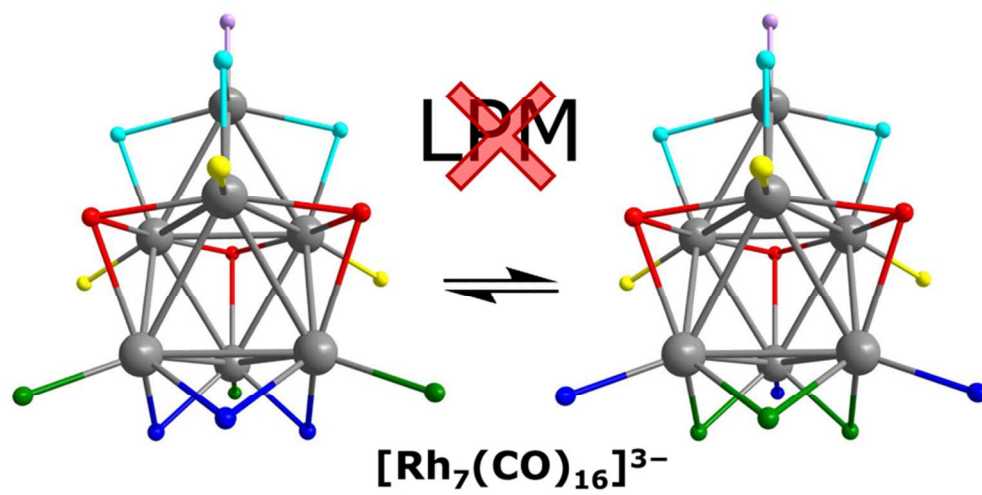


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Use of the LPM to provide a general mechanism for ligand fluxionality in Rh-containing carbonyl clusters in solution is questioned.



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