

Fluxional Organogold Complexes†

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1.0 Introduction

Organogold compounds were among the first transition metal alkyls to be discovered, yet the study of organogold compounds is still in its infancy. The study of organogold compounds is of great importance not only because of their wide applications ranging from electronic industry to medicine, but also because of interesting chemical features shown by these compounds. The latter aspect includes thermal decomposition behaviour of organogold compounds, reactions of gold with olefins and acetylene, and reactions involving cleavage of gold-carbon bonds. Recently, another interesting feature of organogold compounds, their fluxional behaviour, has come into prominence.

The purpose of the present article is to highlight recent trends in the study of fluxional or non-rigidity behaviour of some organometallic compounds, especially those of organogold compounds. It is hoped that the present article will provide impetus for further advances in this exciting area of research.

2.0 Non-rigidity or Fluxionality

If an acceptor molecule A with one free coordination position is confronted with a donor molecule B containing two spatially proximate donor centers, then the acceptor A may not form a bond to only one of the two donor positions of B, but may interact with both the donor centres alternatively. The acceptor A may be taken to be an oscillating acceptor. This concept is in contrast to the widely accepted conventional view of static molecular structures with a single, well-defined nuclear configuration where dynamics and the possibility of intramolecular rearrangements are ignored. However, a number of examples are now known where the molecular vibrations or intramolecular rearrangements carry a molecule from one nuclear configuration into another. When such process occurs at a rate permitting detection by some

physicochemical method, the molecules are designated as *stereochemically nonrigid* or *fluxional*¹⁻³. The fluxional molecules possess more than a single configuration representing an energy minimum on the molecular potential energy surface. Several such minima may be present which are separated by barriers whose dimensions are permissive of rapid passage (tunnelling, thermal excitation over barrier or intermediate cases) of the molecules from one potential well into another under easily accessible conditions.

The choice of a suitable physical method for the study of the fluxional molecules depends on the relationship between the lifetime of a particular molecular structure and the various physical methods. The electron-, neutron- and X-ray diffraction methods (time scale 10^{-18} to 10^{-20} sec) are termed as 'instantaneous' as the interaction between the molecule and the diffracted wave takes place over a period of time that is very short with respect to molecular motions. The conventional spectroscopic methods, e.g. electronic and IR, are much faster than molecular vibrations or interconversions and, the spectrum reflects a weighted average of the species present. Other spectroscopic methods are slower and the time-period of interaction may be comparable to that of the lifetime of the molecule present and hence the nature of changes taking place can be studied by such techniques. It is the technique of NMR spectroscopy that most commonly reveals the occurrence of stereochemical-non-rigidity, as its time-scale is 10^{-1} to 10^{-9} sec. The rearrangements involved in fluxional behaviour are rate processes with activation energies, and when they are in the range of 25 - 100 kJmol⁻¹, the rates of rearrangements can be brought to 10^2 - 10^5 sec⁻¹ at temperatures between $+150^\circ$ and -150° . Thus, by varying the temperature and hence the rapidity of reversible intramolecular rearrangements, the rearrangement processes can be controlled so that they are slow enough at lower temperatures to allow detection of individual equivalent molecules and rapid enough at higher temperatures for the NMR signals from the different environments to be averaged into a single line at the mean position. Lowering of temperature increases the

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complexity of the NMR spectrum and a static configuration 'freezes out'. Thus, variable temperature NMR spectroscopy or dynamic NMR spectroscopy enables the examination of the rearrangement processes in the fluxional molecules in sufficient detail and helps in establishing a mechanism for the rearrangement process.

3.0 Gold Compounds and the NMR Technique

Gold normally exhibits valencies of +I and +III, although examples are known where the oxidation states may vary from -I to +V through +II and other fractional oxidation states⁴. Among the many available physicochemical methods, the NMR technique is of paramount importance in the study of gold compounds. Eventhough, ¹⁹⁷Au has a nuclear spin of 3/2, the associated nuclear quadrupole moment leads to a short relaxation time rendering the ¹⁹⁷Au NMR measurements rather unimportant. However, ¹H, ³¹P, ¹³C and ¹¹B NMR^{5,6} studies of gold compounds are very significant as meaningful conclusions about their structure and other properties may be obtained. In addition to its basic function of locating magnetically active nuclei by the measurement of chemical shift and spin-spin coupling parameters, NMR is extensively used in contemporary research for studying molecular motions and chemical exchange.

4.0 Types of Fluxional Molecules

4.1 Simple Organic and Inorganic Compounds

The fluxional molecules may be purely organic, purely inorganic, organometallic or organometalloidal ones³. The fluxional organic molecules may range from common molecules like cyclohexane to other exotic molecules such as those undergoing 'degenerate cope arrangements'⁷. The fluxional inorganic molecules may be penta- (e.g. PF₅)^{8,9}, hepta- (e.g. IF₇)¹⁰, octa- (e.g. Mo(CN)₈⁴⁻)¹⁰ or nona- (e.g. ReH₉²⁻)¹¹ coordinate species with life-times between 10⁻³ and 10⁻¹² sec. For illustration, the case of simple PF₅ may be considered, which on the basis of IR spectral and electron diffraction data is shown to have a trigonal-bipyramidal (TBP) geometry in the ground state. However, its ¹⁹F NMR spectrum consists of a single doublet (*J*_{PF}, 916 Hz) down to -160°C; due to a fast intramolecular process that exchanges axial and equatorial fluorines. The accepted mechanism for this exchange process is Berry pseudo-rotation where the transition state is probably square-pyramidal (SP)¹², and the rearrangement process leaves the molecule in a restricted, permuted form of its original state. The rate constant and activation energies of pseudo-rotation in PF₅ are estimated to be 1.7 × 10⁷ sec⁻¹ and 7.9 kcal/mol, respectively, at 27°C.

4.2 Coordination Compounds

The octahedron is an excellent coordination polyhedron and yet molecules in this configuration are also known to exhibit non-rigidity phenomenon. Variable temperature NMR spectra show that in the β-diketonate complexes of Ti(IV), e.g. Ti(acac)₂X₂ (acac = acetylacetonate anion; X = F, Cl, Br)¹³, (1), the acetylacetonate rings undergo rapid configurational changes which exchange acetylacetonate methyl groups between the two non-equivalent sites of the *cis*-isomer. At higher temperatures fast intramolecular rearrangement renders all the methyl groups magnetically equivalent, but at low temperatures two-distinct methyl signals are registered (Fig. 1). The first-order rate constants, extrapolated to 25°C, for exchange of the methyl groups, activation energies and enthalpies of activation have been determined to be, respectively, 1.6 × 10¹⁴ sec⁻¹, 11.6 ± 0.5 kcal/mol and -2.4 ± 2.3 eu (X = F); 6.7 × 10² sec⁻¹, 11.2 ± 0.6 kcal/mol and -10.0 ± 2.3 eu (X = Cl); 2.3 × 10³ sec⁻¹, 11.6 ± 0.4 kcal/mol and -6.3 ± 1.6 eu (X = Br).

Similar observations have been also made for the dialkoxide complex, *cis*-Ti(acac)₂(OR)₂¹⁴ and *cis*-M(acac)₂Cl₂ (M = Sn, Zr) complexes where exchange process results in temperature-dependent collapse of the two methyl resonances. The double alkoxide bridged bioctahedral (edge shar-

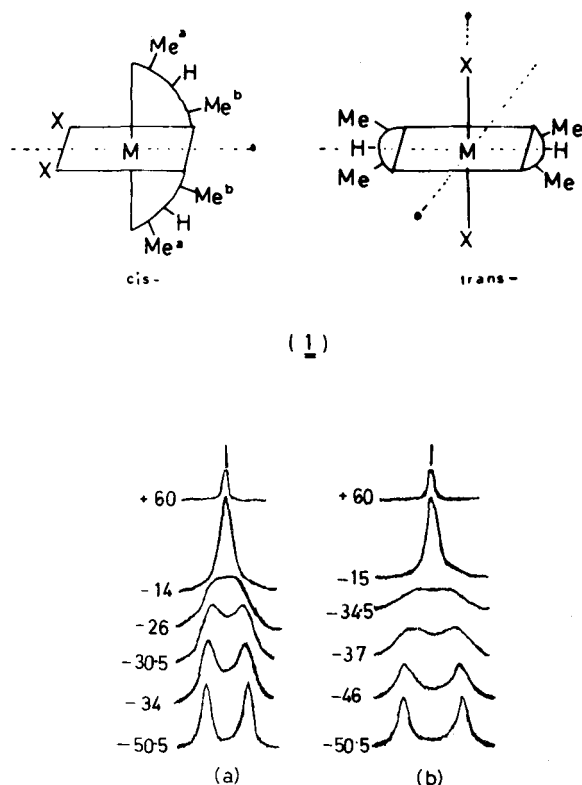


Fig. 1—Partial PMR (methyl region) spectra of (a) Ti(acac)₂Cl₂ and (b) Ti(acac)₂Br₂ in CD₂Cl₂ at different temperatures.

ed) structure of dimeric pentaalkoxides, $M_2(OR)_{10}$ ($M = Nb, Ta$; $R = Me, Et, Bu$) (2) is shown to be a simple example of non-rigid structures on the basis of variable temperature NMR spectroscopy¹⁵, where rapid intramolecular double exchange of alkoxide groups occurs between the two types of terminal groups and the terminal and bridging groups. The NMR at 100°C in octane has only a single averaged methyl 1H signal. Below 40°C, two signals in the intensity ratio of 1:4 are seen due to the averaging of the t_2 and t_1 protons. At -58°C three clear signals in the intensity ratio 1:2:2 are registered. Addition of CH_3OH results in a separate CH_3 resonance and thus the exchange of t_1 , t_2 and b sites is clearly an intramolecular process.

4.3 Elementoorganic and Organometallic Compounds

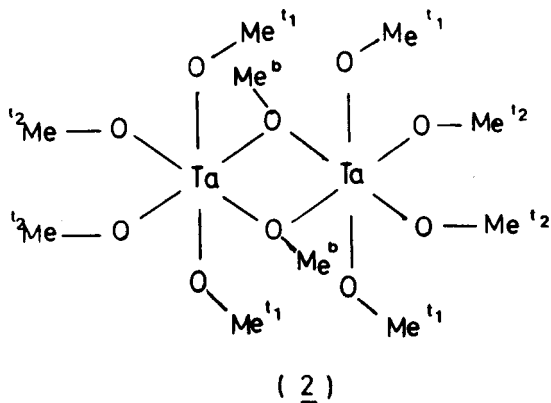
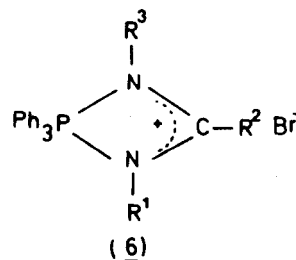
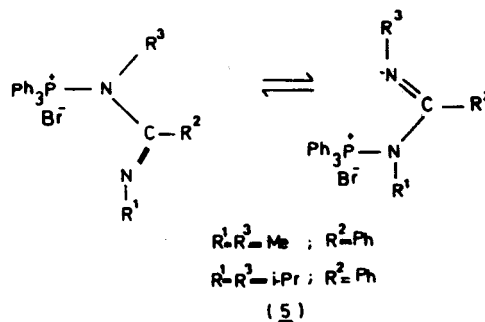
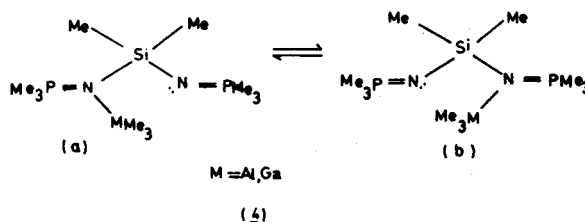
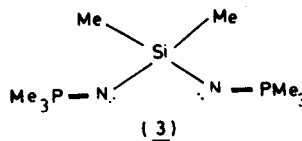
Schmidbaur and Wolfsberger¹⁶ observed that the compound $Me_2Si(NPMe_3)_2$ (3) when reacted with Me_3Al or Me_3Ga gave compound (4) whose NMR in CH_2Cl_2 or C_6H_6 at room temperature showed only one signal each for the protons of the methyl groups attached to the silicon and to the metal atom, and one doublet for the protons of Me_3P groups. On lowering the temperature, the Me_3P doublet becomes broader and eventually splits into two doublets. Since the singlet signals of Me_2Si and Me_3M are retained at all temperatures, this phenomenon is due to a temperature dependent exchange process $4a \rightleftharpoons 4b$. The phenomenon is fully reversible and can be repeated *ad infinitum*. The interchange of positions of the metal atom may be due to intermediate complete dissociation of the donor atom from the acceptor or might occur through a transition state containing penta-coordinated metal.

In contrast, the NMR spectrum of the corresponding Me_3In complex down to -70°C gives a temperature-independent NMR spectrum with one Me_3P doublet only indicating either a rigid pentacoordinate structure or an extremely rapid exchange phenomenon where the activation energy of

jump is less than 8 or 9 kcal/mol. The tetracoordinate complexes of 3 with Me_2Zn and Me_2Cd have, however, a rigid structure at all temperatures.

The NMR spectra¹⁷ (Fig. 2) of amidinotriphenylphosphonium salts (5) establish their fluxional character. The rearrangement process might be taking place through the structure (6) with a quinquelignant phosphorous. Fluxional behaviour by way of 1,3-wandering shift of the Me_3Si group has been reported in N,N -bis(trimethylsilyl)methane sulphonamide, $(Me_3Si)_2NS(O)Me$, which is converted to the tautomeric imide, $Me_3SiNS(OSiMe_3)Me$ ¹⁸.

The non-rigidity phenomenon is, however, more common in certain types of organometallic compounds. This phenomenon is characteristically encountered in compounds containing conjugated cyclic polyolefins such as cyclopentadienyl, cycloheptadienyl or cyclooctatetraene and also the allyl group. Literature is abundant with the examples of fluxional organometallic molecules of this type^{3,19,20}. Before dealing in detail with the fluxional behaviour of



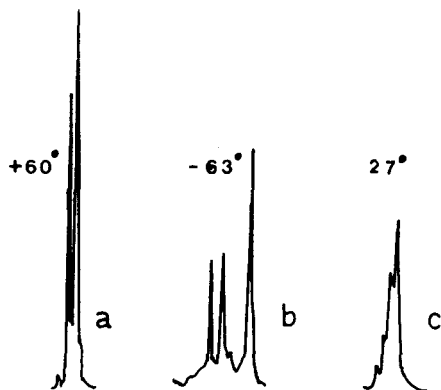


Fig. 2—Partial PMR (methyl region) spectra of amidinophosphonium bromide (5a) in CDCl_3 at different temperatures.

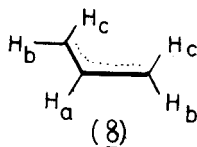
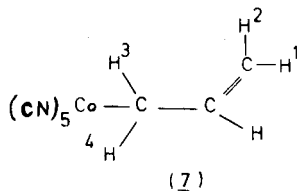
typical gold compounds, for the sake of an overview as well as for illustration, only some typical examples of fluxional organometallic complexes will be considered.

4.31 Allylic complexes

An allyl group may be either σ -bonded to a metal atom, $\text{M}-\text{CH}_2-\text{M}-\text{CH}_2-\text{CH}=\text{CH}_2$ or π -bonded. An example of a compound containing a metal- σ -allyl bond²¹ is $[(\text{NC})_5\text{Co}-\text{CH}_2-\text{C}(\text{H})=\text{CH}_2]^{3-}$ (7), whose NMR shows that protons 3 and 4 are magnetically equivalent, while protons 1 and 2 are not.

The π -allyl radical gives three major resonance peaks corresponding to the three types of protons as shown in (8). The relative intensity ratio is 1:2:2. The H_a ($\delta > \delta > \delta > 4$ ppm) is the least shielded and under high resolution gives a pattern of overlapping triplets because of the splitting by the two equivalent pairs of protons H_b and H_c . The resonance signals for H_a at δ 3.4–4.4 ppm and H_c at δ 2.2 ppm are well separated and generally appear at higher fields.

Most π -allyl groups, e.g. $\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_4$, exhibit spectra of an $\text{A}_2\text{M}_2\text{X}$ system, and some exhibit spectra typical of an A_4X system where the allyl group has equivalent terminal hydrogens. Some allyl complexes, e.g. $(\text{C}_3\text{H}_5)_4\text{Zr}^{22,23}$, $(\text{C}_3\text{H}_5)_4\text{Th}^{24}$, $(\text{C}_3\text{H}_5)_4\text{Rh}^{25}$, $(\text{C}_3\text{H}_5)_2\text{M}(\text{M}=\text{Ni}, \text{Pd}, \text{Pt})^{23}$ and $[(\text{C}_3\text{H}_5)_2\text{RhCl}]_2^{26}$,



show the π -allyl spectra, $\text{A}_2\text{M}_2\text{X}$, at lower temperatures and the A_4X spectra at higher temperatures. This fluxional behaviour arises as each of the four terminal protons passes through the two available environments rapidly. At low temperatures it would typically give a spectrum as shown in Fig. 3(a). The two large doublets represent the two hydrogen atoms (H_b) in *syn*- or *cis*-positions and the two hydrogen atoms (H_a) in *anti*- or *trans*-positions relative to the fifth hydrogen (9). The multiplet represents the fifth hydrogen split by the other four. With the increase in temperature, the spectrum in Fig. 3(a) changes to that in Fig. 3(b), in which the two doublets have collapsed into one, indicating that on a time average basis there are only two types of hydrogens, namely the four terminal hydrogen atoms that are equivalent and one nonterminal hydrogen. This fluxional behaviour results from the molecule rapidly interconverting, the pathway being $\eta^3-\eta^1-\eta^3$ process.

4.32 Cyclopentadienyl complexes

The cyclopentadienyl radical may be either π - or σ -bonded to the metal atom. Due to rapid rotation about the metal-ring axis the protons in a complexed π -cyclopentadienyl ring system appear to be essentially equivalent. Since the original work of Wilkinson and Piper²⁷ on the NMR behaviour of $(\text{C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2$, which on the basis of X-ray crystallographic structure analysis was shown to be $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\sigma\text{-}$

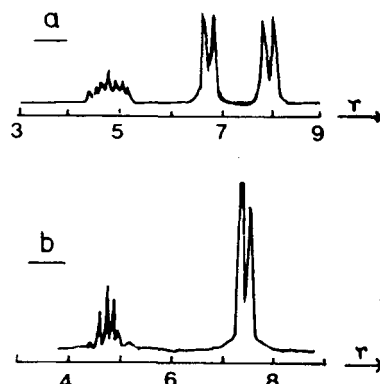
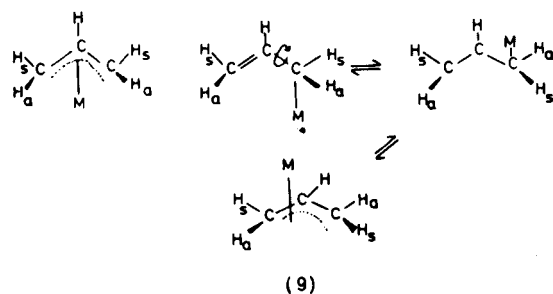


Fig. 3—Typical PMR spectrum of (a) trihapto-allyl system at low temperatures and (b) fluxional-allyl system indicating time averaging of the four terminal H 's.

C_5H_5)²⁸, a number of cyclopentadienyl complexes have been characterised as fluxional molecules. The NMR spectrum of this compound in CS_2 solution between -80° and -100° shows only one signal for the $\pi-C_5H_5$ group and an AA'BB'X spectrum for the $\sigma-C_5H_5$ group. The A and B multiplets appear at about $\delta 6.0$ - 6.3 ppm and the X-signal appears at about $\delta 3.5$ ppm. Essentially, a similar NMR pattern for the $\sigma-C_5H_5$ group was observed for $(\pi-C_5H_5)Cr(NO)_2(\sigma-C_5H_5)$ ²⁹. The low-field part of the AA'BB' multiplet pattern is assigned to the A-protons and the higher-field part to the B-protons. At higher temperatures the three signals coalesce to one signal for both the Fe and Cr compounds. However, the low-field part of the AA'BB' pattern broadens more rapidly than the high-field one. This asymmetric coalescence indicates the absence of intermolecular exchange of σ -cyclopentadienyl groups. There are two reaction paths presumably leading to asymmetrical broadening of the AA'BB' multiplet, namely, the 1,2-shifts and the 1,3-shifts (10).

4.33 Cyclopolyene complexes

Often a cyclopolyene forms a complex with a metal such that some but not all of the π -electrons are involved in bonding. Such a molecule is most likely to be fluxional. An interesting observation is made in the NMR study of cyclooctatetraene iron tricarbonyl, $(C_8H_8)Fe(CO)_3$ ³⁰. A planar structure for the cyclooctatetraene (COT) part was postulated on the basis of a sharp singlet NMR signal at room temperature. The X-ray crystal structure³¹ revealed a non-planar 1,3-diene bonding (of π -butadiene type) mode of the COT, which was later confirmed by the variable temperature NMR spectrum down to $-150^\circ C$. These results have been explained on the basis of a 'ring-whizzing' process resulting from a series of 1,2-shifts involving concomitant migration of double-bond character within the ring (11,12). The Cr

and Mo analogues behave similarly^{32,33}, where the frozen structures appear at about -40° . Both $(C_8H_8)Mo(CO)_3$ and $(C_8H_8)Cr(CO)_3$ display one sharp resonance at $+80^\circ$ and multiplet pattern at -40° (Fig. 4).

Fluxional behaviour³⁴ of cycloheptatrienylmanganese tricarbonyl and cycloheptatrienyl iron tricarbonyl cations has been reported. The NMR spectra of both the isoelectronic species show a difference of 3-8 kcal/mol in their activation energies for the fluxional processes.

5.0 Fluxional Organogold Compounds

5.1 Acetylene, Cyclopentadienyl and Benzene Complexes

The interaction of acetylenes with gold halides leads³⁵, in the case of dimethylacetylene, to the formation of π -complexes (13) which, however, rearrange to the σ -complexes such as (14) under mild acidic conditions.

Pure (not complex stabilised) alkylgold compounds of the type RAu have not yet been isolated. However, the number of complexes derived therefrom is steadily increasing. The cyclopentadienyl complexes, which have been shown to possess a fluxional structure with an $Au-C$ bond, warrant special mention³⁶. The cyclopentadienyl(triphenylphosphine)gold(I), and the corresponding methylcyclopentadienyl(triphenylphosphine)gold(I), (15), $(RC_5H_4)Au(PPh_3)$ ($R = H$ or

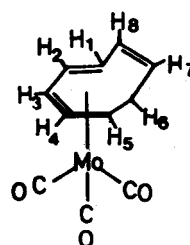
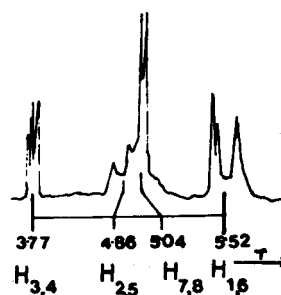
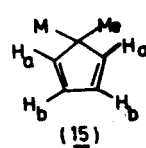
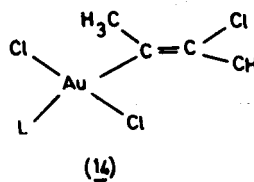
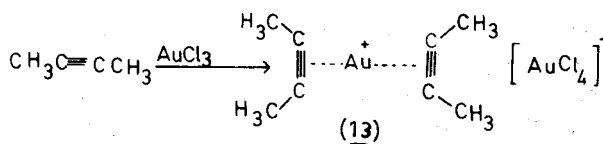
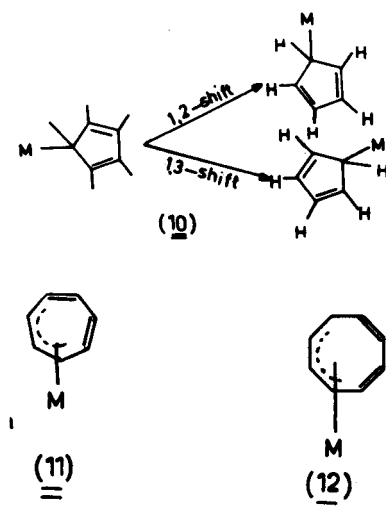
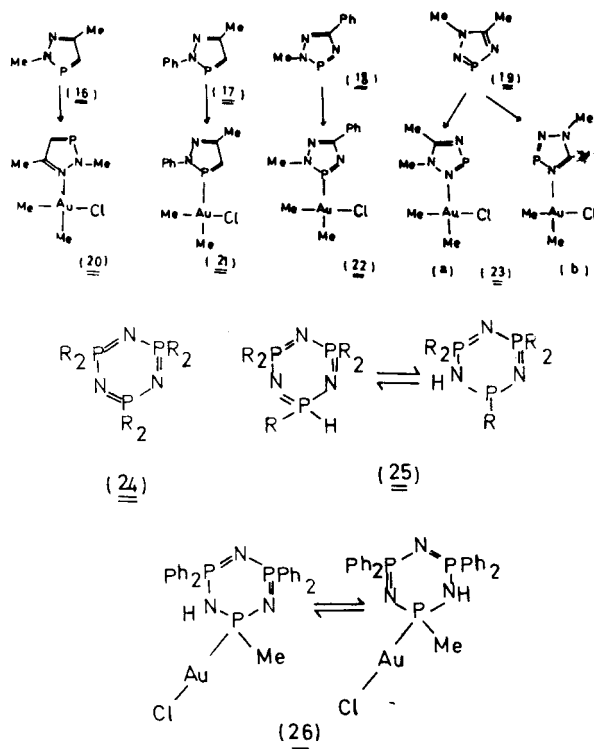


Fig. 4—Low temperature PMR spectrum of $C_8H_8Mo(CO)_3$ with assignments.

Me), have been synthesised and their NMR spectra at room temperature and at low temperatures have been reported³⁷⁻³⁹. The compounds are suggested to have monohapto (i.e. σ -bonded) rings in contrast to the corresponding Cu(I) derivative which has a π -bonded structure in the solid⁴⁰ state persisting in all but the most polar solvents⁴¹. The compound $(C_5H_5)Au(Ph_3P)$ has a single sharp NMR absorption at temperature down to -50° which broadens at lower temperatures and then splits into a doublet, arising from coupling with the ^{31}P nucleus, with a separation of 2.8 Hz at -75° (in 2-methyltetrahydrofuran). The individual components of this doublet show no signs of broadening even at -100° , and assuming a σ -bonded structure for the compound it seems that the exchange is still fast at this temperature. The absence of any splitting at higher temperatures is evidently due to an intermolecular exchange process³⁸. In the presence of about three equivalents of added Ph_3P , the spectrum remains a singlet even at -100° indicating exchange of phosphine molecules and the fact that free phosphine increases the exchange rate. The analogous $(MeC_5H_4)Au(Ph_3P)$ compound gives two ring proton signals at δ 5.98 and 5.73 ppm at room temperature where the highfield resonance corresponds to the protons β to the methyl group. This signal broadens on lowering the temperature to about -60° and appears as a resolved doublet with splitting of 4.8 Hz at -90° . On the other hand, the low field signal is not split even upto -100° . There is thus a considerable difference between the J_{PH} corresponding to these two resonances which can be rationalised on the basis of a rapidly rearranging σ -bonded structure. This compound is thus σ -bonded at least in 2-methyltetrahydrofuran. The difference from analogous Cu(I) compound, which is π -bonded in ethers, is in accordance with the well-known tendency of gold(I) to form linear two-coordinate complexes.

5.2 Organogold Complexes with Five-membered Di- and Tri-azaphospholes

The azaphospholes (16-19), 2,5-dimethyl- and 5-methyl-2-phenyl-1,2,3 σ^2 -diazaphospholes (16 and 17 respectively), and 2-methyl-5-phenyl- and 1,5-dimethyl-1,2,4,3 σ^2 -triazaphospholes (18 and 19 respectively), contain potential donor atoms in positions 1,2 or 1,3 and hence complexes of these ligands are likely to exhibit fluxional behaviour. These di- and tri-azaphospholes react in CH_2Cl_2 medium with dimethylgold chloride at $-20^\circ C$ to form discrete 1:1 adducts (20-23), which can be isolated as white powders⁴². According to their 1H NMR spectra, the complexes contain tetracoordinate square-planar gold with the two CH_3 groups exclusively *cis*- to each other, *cis*- $Me_2AuCl(L)$. Such complexes give rise to two CH_3



signals of equal intensity, the resonance at lower field being assigned to the methyl group *trans* to the donor ligand L^{43} . Both chemical shifts are almost equally sensitive to the nature of L e.g. with pyridines the signal tends to appear at low field than that with phosphines. Thus, the ligands 16 and 19 coordinate through the N-end whereas the ligands 17 and 18 coordinate through their P-end. Further, each methyl group on Au is split into doublets by a typical three-bond 1H - ^{31}P coupling in 21 and 22 which is also confirmed by $^1H\{^{31}P\}$ decoupling experiments. The NMR spectra of the complexes (Fig. 5) do not change with change in temperature, suggesting the unaltered mode of coordination and absence of fluxional behaviour. In these cases, it seems that the coordination of the ligands is guided by the inductive effect of the substituents rather than by the specific donor properties of the donor atom N or P.

5.3 Organogold Complexes with Six-membered Pentaorganocyclotriphosphazene

The cyclotriphosphazenes are an unusual class of ligand molecules, the chemistry of which has attracted attention in recent years⁴⁴. The classical cyclotriphosphazenes, 24, with six electronegative or organo substituents can function only as N-donors whereas the novel class of PH-function cyclotriphosphazenes⁴⁵⁻⁴⁷, 25, has an additional coordination site at P- in a tautomeric NH-form. The reaction of this ligand with $(CO)AuCl$ in CH_2Cl_2 results⁴⁸ in the linear, 2-coordinate $L-Au-Cl$ complex, 26. In the

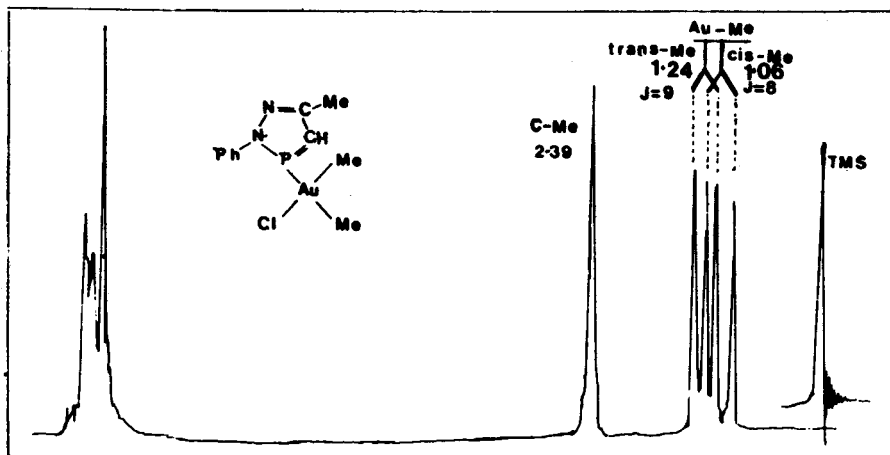
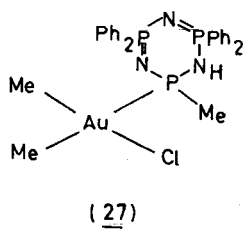


Fig. 5—PMR spectrum of $[\text{Me}_2\text{AuCl}(5\text{-Me-2-Ph-1,2,3-}\sigma^2\text{-diazaphosphole})]$ in CDCl_3 .

IR-spectrum of the complex, the $\nu(\text{PH})$ absorptions of the free ligand **25** occurring at 2310 and 2360 cm^{-1} disappear and are replaced by weak $\nu(\text{NH})$ absorptions at 3160 cm^{-1} . The ^{31}P NMR signal due to P-2 is strongly shifted towards low-field on complexation (δ 66.8 ppm for the complex as against δ 6.9 ppm for the free ligand). This clearly proves P-coordination of the ligand.

The above conclusion is supported by the findings of temperature dependent NMR spectroscopy. The ^1H NMR spectrum exhibits a PCH_3 doublet resonance at δ 2.75 ppm ($^2J_{\text{PH}} = 10.5$ Hz), which is independent of temperature, and a complex C_6H_5 multiplet. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum has a corresponding PCH_3 doublet at δ 31.25 ppm ($^1J_{\text{PC}} = 46.9$ Hz) at 30°C, with little change at -60°C . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is clearly temperature dependent, and contains a triplet/doublet AX_2 pattern at 30°C, which changes to an AXY spin system at -80°C (Fig. 6). At 30°C the two $(\text{C}_6\text{H}_5)_2\text{P}$ phosphorus atoms are thus equivalent on the NMR time scale, but become non-equivalent below -40°C (in CDCl_3 or CD_2Cl_2). This observation can be explained through a tautomerism of the type **26a** $\rightleftharpoons$ **26b**, where the proton rapidly fluctuates from one N atom to the other.

The reaction of $[\text{Me}_2\text{AuCl}]_2$ and the ligand **25** in CH_2Cl_2 at -20°C results⁴⁸ in the square-planar, four-coordinate complex, $\text{Me}_2\text{Au}(\text{L})\text{Cl}$, **27**. In the ^1H NMR spectrum of this complex, presence of two doublet

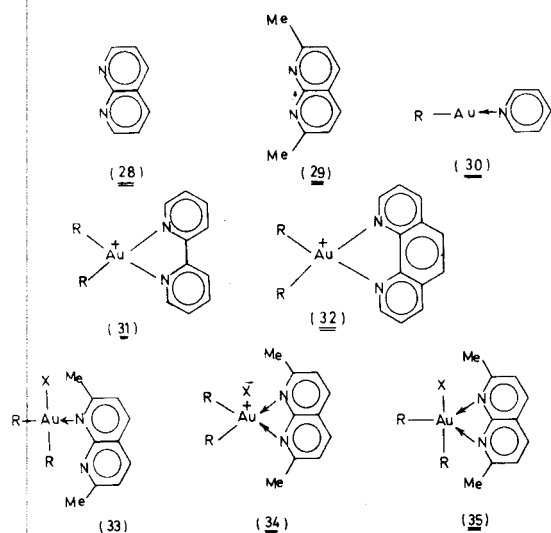


signals of CH_3Au groups indicates the *cis*-configuration at the metal centre and also a $^1\text{H}-\text{C}-\text{Au}-^{31}\text{P}$ coupling through the $\text{Au}-\text{P}$ linkage. The ^{31}P decoupling experiments, $^1\text{H}\{^{31}\text{P}\}$, confirm the assignments and the ^{13}C NMR data complement the conclusions by showing two CH_3Au signals with different *cis*- and *trans*- $^{13}\text{C}-\text{Au}-^{31}\text{P}$ couplings, $J = 4.9$ Hz (*cis*) and $J = 157.2$ Hz (*trans*). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are unexpected in that the non-equivalence of the $(\text{C}_6\text{H}_5)_2\text{P}$ groups is already obvious at room temperature (Fig. 7). Thus, the proton exchange is much slower in **26** than it is in **27**. Increasing the probe temperature resulted in decomposition of the samples and hence the possible equivalence at higher temperature was difficult to ascertain. Nevertheless, the fluxional behaviour is firmly established for the Au(I) complex, **26**, and the Au(III) complex, **27**.

5.4 Organogold Complexes with a Heterocyclic Ligand with Two Fused Pyridine Rings, 2,7-Dimethyl-1,8-Naphthyridine (DMN)

Naphthyridines (**28**) are an interesting class of ligands with 1,3-bisimino donors where the two donor atoms (N's) are in close proximity and therefore the complexes are expected to show the characteristics of nonrigid molecules similar to those found for other monofunctional acceptors and 1,3-difunctional donors^{16,49}. Dialkylgold derivatives form stable non-ionic complexes with pyridine (**30**) and the ionic, chelated species (**31**) and (**32**) with 2,2'-bipyridyl and 1,10-phenanthroline, respectively. With naphthyridine, two possible structures (**33**, **34**) with a four-coordinate Au(III) centre are expected in addition to the less common five-coordinate⁵⁰ Au(III) compound, (**35**).

The chelate interaction in (**34**) and (**35**) would require a highly strained four-membered ring system, since the



nitrogen lone pair electrons are in orbitals parallel to each other and would, therefore, interact less favourably with the gold orbitals. The close proximity of a second donor site in structure (33) should result in very low activation energies for an intramolecular 1,3 shift of the gold atom similar to the 'oscillation' found in some complexes of Al, Ga and In alkyls¹⁶, as well as for analogous Si, Ge⁴⁹ and phosphorus compounds^{17,18}, with 1,3-bisimino donors⁵⁰ (Eq. A). The ligand 2,7-dimethyl-1,8-naphthyridine⁵¹, rather than the simple ligand 1,8-naphthyridine, is helpful in the evaluation of the NMR spectrum as the possible nonequivalence of the two fused pyridine rings can be easily detected by the nonequivalence of the two methyl resonances.

At room temperature, the ¹H NMR spectrum of (33) has two equivalent ligand CH₃ groups but two nonequivalent *cis*-AuCH₃ groups, with a single AB pattern for the two equivalent sets of aromatic

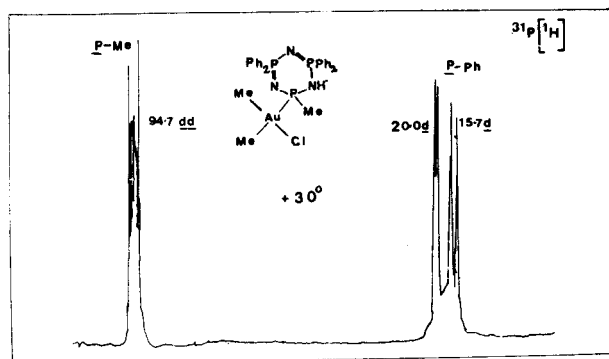


Fig. 7—³¹P NMR (¹H decoupled) spectrum of [Me₂AuCl(2-Me-4,4,6,6-tetraphenylcyclotriphenylphosphazene)] in CD₂Cl₂.

protons. The spectra recorded in various solvents, such as benzene, toluene, dichloromethane and chloroform are identical, with the number and relative intensities of peaks remaining unaltered. This result is compatible with either a dihapto, pentacoordinate structure, where both the N atoms of the ligand DMN are coordinated to Au(III) along with the X group and two CH₃ groups, or with the four-coordinate, square-planar structure if the equilibrium 33(a)⇌33(b) (Eq. A) is assumed. At higher temperatures (~60°C) the nonequivalence of the *cis*- and *trans*-CH₃ groups on Au is no longer preserved and the signals broaden and coalesce. This is clearly due to a rapid ligand exchange which renders the CH₃ groups on Au equivalent. Both X and DMN of (CH₃)₂Au(DMN)(X) may be involved in this process^{52,53}. Intermolecular

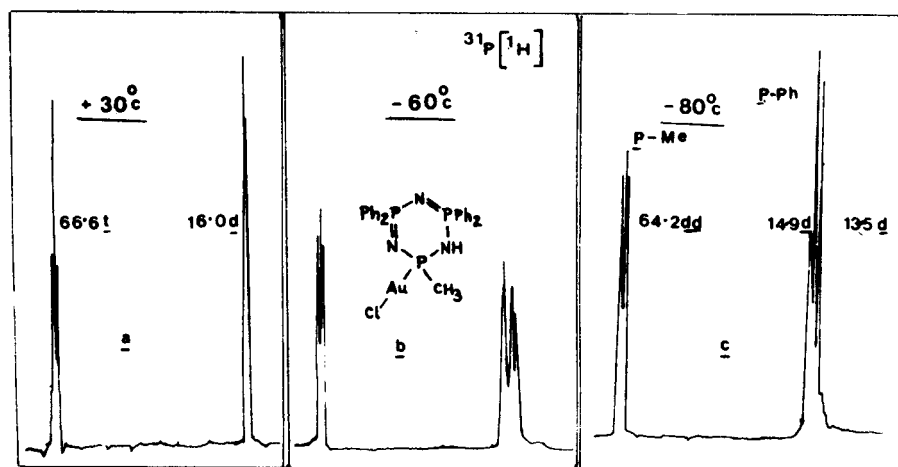
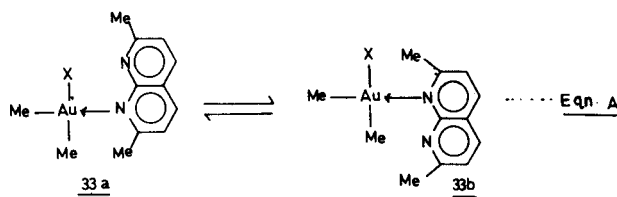
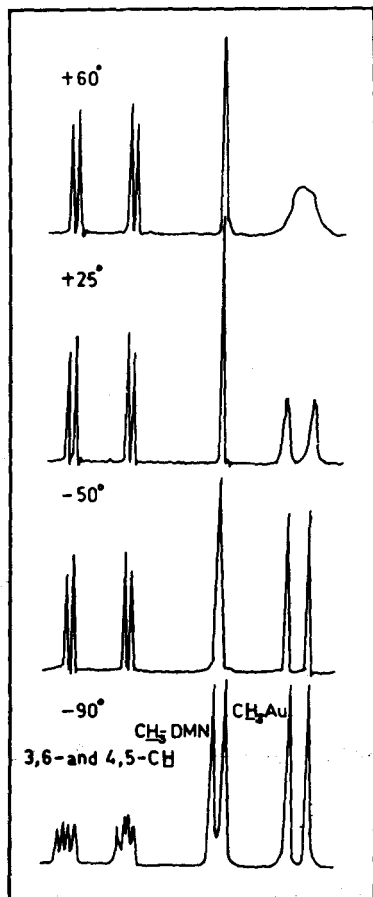


Fig. 6—³¹P NMR (¹H decoupled) spectrum of [AuCl(2-Me-4,4,6,6-tetraphenylcyclotriphenylphosphazene)] in CD₂Cl₂ at (a) +30°C (b) -60°C and (c) -80°C.

Table 1—Coalescence Temperature, Shift Differences and Activation Energies for Intra- & Inter-molecular Exchange Processes (from Variable Temp. ^1H NMR Spectra)

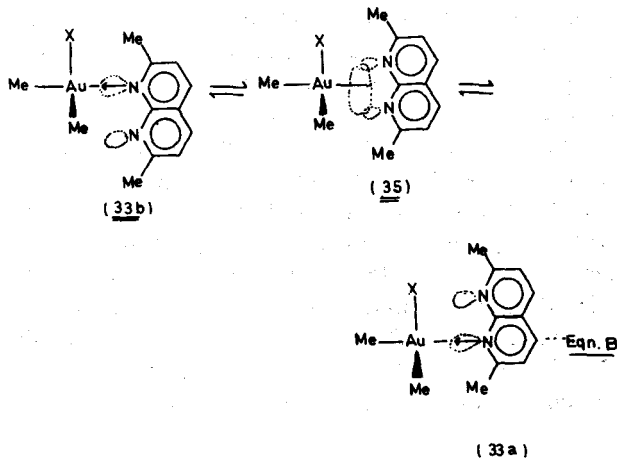
Compound $\text{Me}_2\text{Au}(\text{DMN})\text{X}$ $\text{X} =$	Intramol. DMN site exchange			Intermol. (pseudo)halide exchange		
	T_c	ΔH , Hz	$\Delta G^\ddagger$ (kcal/mol)	T_c	ΔH , Hz	$\Delta G^\ddagger$ (kcal/mol)
Cl	-63	17	10.61	+70	42	17.16
Br	-65	15	10.56	+60	36	16.64
I	-70	15	10.30	Dec.	33	
OCN	-73	16	10.11	+76	54	16.90
SCN	-72	15	10.19	+65	16	17.44
SeCN	-66	14	10.54	+50	25	16.35

Fig. 8—PMR spectrum of $\text{Me}_2\text{Au}(\text{DMN})\text{Cl}$.

exchange studies, even in presence of extra DMN ligand, for the $(\text{CH}_3)_2\text{Au}(\text{DMN})(\text{X})$ unambiguously prove that the exchange of DMN ligand is slow on the NMR time scale and that the exchange of X, the halide or pseudohalide, is predominantly responsible for the coalescence of the *cis*- and *trans*- CH_3 signals on Au.

At low temperatures, below -60°C , the signals of DMN ligand protons broaden and split into pairs and at -90°C , two singlets of equal intensity are registered for the CH_3 groups of DMN, alongwith two AB quartets, also of equal intensity, for the aromatic protons in the 3,4 and 5,6 positions, respectively (Fig. 8). From the individual coalescence temperature,

which depends only slightly on the nature of halide or pseudohalide substituent, being lowest for OCN and highest for Cl, and the chemical shift differences of the nonequivalent DMN- CH_3 signals at -90° (Table 1), the activation energies for the process according to Eq. (A) have been calculated⁵⁴. The $\Delta G^\ddagger$ values have also been estimated from the coalescence of $(\text{CH}_3)_2\text{Au}$ signals. The NMR experiments clearly establish a distinct fluxional behaviour of these non-ionic, molecular organogold complexes. At very low temperatures the Au centre is associated with only one of the two N donors of the ligand and there is a rapid intramolecular two-site exchange at elevated temperatures through the pentacoordinated transition state (35) (Eq. B).



For $\text{Au}(\text{III})$, interaction with a single ligand orbital is favoured, as shown in 33(a) and 33(b) (Eq. B), in comparison with bonding through two closely spaced orbitals of difunctional donor as in (35). Although this symmetrical interaction is higher in energy, it is a favourable transition state or intermediate for the observed intramolecular rearrangement according to (Eq. B), i.e. $33(\text{a}) \rightleftharpoons 33(\text{b})$. This mechanism is far superior to a largely intermolecular dissociation-recombination mechanism, as shown by the differences in the activation energies of both the processes (Table 1).

5.5 Organogold Complexes with Difunctional Thiopethers Containing Pyramidal Sulphur

The study of pyramidal inversion of N atoms is a common example of the dynamic NMR technique and much information is available on the energetics of this process⁵⁵⁻⁵⁷, whereas other group 5A elements exist, in general, in pyramidal configurations too stable to allow the NMR studies. Among group 6A elements, oxygen tends to invert too rapidly and S, Se and Te too slowly with respect to the NMR time scale. However, the bonding of S, Se and Te to transition metals accelerates the rate of inversion and makes it amenable to detection by NMR techniques⁵⁸⁻⁶¹. As an example, it is seen that the coordination of organic sulphides to transition metals produces species wherein the inversion barrier at sulphur is lowered to the 20-80 kJ mol⁻¹ range thus making these especially suitable for investigation by the dynamic NMR technique^{58,60}.

A good example of the inversion at S atom in complexes is provided by AuCl and AuCl₃ complexes with dibenzylsulphide, (PhCH₂)₂S⁶². The ¹H NMR signal of the CH₂ protons in [(PhCH₂)₂SAuCl₃] appears as an AB quartet since the two hydrogen atoms on each benzyl group are non-equivalent due to the lack of a plane of symmetry containing the S-C bond. In turn, this is due to the pyramidal structure of sulphur which has a stereochemically active lone pair of electrons. At temperatures above 62°C, the AB quartet collapses to a single peak since at high temperatures inversion at the S centre occurs rapidly on the NMR time scale making the protons appear equivalent. Measurement of spectra at different temperatures allows the activation parameters to be calculated. Inversion at sulphur is much faster in [(PhCH₂)₂SAuCl] than in [(PhCH₂)₂SAuCl₃] complex and even at low temperatures only a singlet for the CH₂ protons is obtained for the Au(I) complex.

Dimethylgold halides and pseudohalides, Me₂AuX (X=Cl, Br, I, NCS), react⁵² with 1,2-bis(alkylthio)ethane, RSCH₂CH₂SR (R=Me, Et) and 1,2-

bis(alkylthio)propane, RSCH₂CH₂CH₂SR (R=Me, Et) to form complexes of the type (36). At room temperature the CH₃ groups on gold give a sharp signal at ~δ 1.35 ppm, but at low temperature (~ -20°C) this signal splits into two with a separation of about 0.40 ppm due to the presence of two non-equivalent *cis*- and *trans*-methyl groups on gold. The S-CH₃ signals remain unchanged using dimethylgold-nitrate, Me₂Au(NO₃), and CH₃SCH₂CH₂SCH₃; a chelated 1:1 complex and not a bridged one (37) is obtained, the NMR spectrum of which shows unexpected dependence on temperature. At room temperature (30°C) three sharp signals are obtained at δ 1.47, 2.72 and 3.79 ppm in the intensity ratio of (6:6:4) corresponding to CH₃Au, CH₃S and CH₂ protons. However, on lowering the temperature to about -30°C the methyls on Au appear at δ 1.52 and 1.48 ppm, the methyls on S at δ 2.93 and 2.67 ppm and the CH₂ protons appear as a complex multiplet at δ 3.80 ppm (Fig. 9). The coalescence temperature, T_c, is -25°C for SCH₃. From the chemical shift difference of 26 Hz (at 100 MHz) and from the splitting temperature of -30°, the free energy of activation for S-inversion is calculated to be 12.15 kcal/mol⁵⁴. All these observations can be explained assuming an inversion process on the S atom of the ring system as shown in Eq. C.

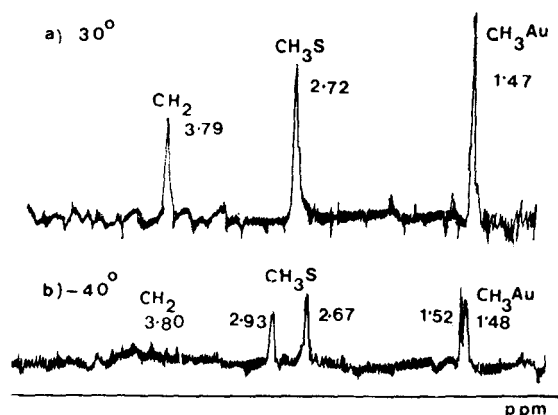
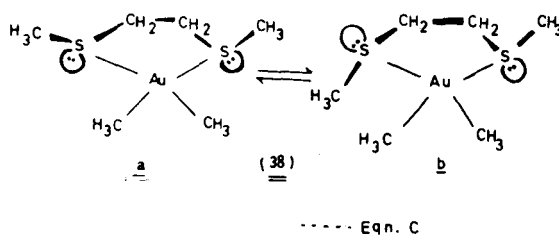
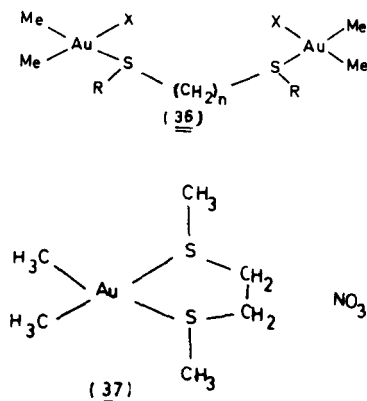


Fig. 9—100.1 MHz PMR spectrum of [Me₂Au(CH₂SCH₃)₂]⁺ NO₃⁻ in CHCl₃ at (a) 30° and (b) -40°. (The CH₂ signal in (b) is so strongly split that it is virtually lost in the base line).



6.0 Conclusion

Dynamic NMR measurements have been used to establish the fluxional behaviour of organogold complexes containing acetylene and cyclopentadienyl groups as ligands. In addition, a series of novel ligands containing donor atoms in 1,2- or 1,3-positions were reacted with Au centre with a hope of observing the same behaviour. Contrary to expectations, fluxional behaviour was not observed for the di- and triazaphosphole complexes of gold. However, with pentaorganocyclotriphosphazene complexes, the rapid fluxional behaviour of the protons was established on the basis of the variable temperature proton decoupled ^{31}P NMR spectra. The organogold complexes with dimethylnaphthyridine (DMN), $[\text{Me}_2\text{Au}(\text{DMN})\text{X}]$, exhibited simple fluxional behaviour where the gold atom oscillates between N-1 and N-8, as is established by variable temperature ^1H NMR spectroscopy. Research in this area is expected to be diversified with the design and synthesis of newer ligands which may form unique complexes exhibiting this behaviour.

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