dizes iodide ion to iodine and triphenylphosphine to triphenylphosphine oxide. Scheme I summarizes some other reactions of **4** which have been studied.[11] All reactions were carried out in THF solution. With the alcohols and with water, exothermic reactions at room temperature were observed. In the case of the reaction with methyllithium, higher oligomers, up to THF-insoluble-polymer, were formed. These must have resulted from attack of the intermediate lithium reagent, $Me_3SiC(CH_3)_2C(CH_3)_2Li$, at the silacyclopropane ring.

For all new compounds combustion analyses and spectroscopic data were obtained which were in full agreement with the structures indicated.

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(8) NOTE ADDED IN PROOF. A referee has suggested that to assess steric vs. electronic factors 1,1,2,3-tetramethyl-2,3-dilsopropylsllirane or 1,1-dimethyl-2,2,3,3-tetraethylsilirane would be better compounds than hexamethylsilirane for the comparison with **2**. Although hexamethylsllirane is somewhat less hindered than **2**, we feel it is a reasonably good first approximation for the purpose under discussion.The two compounds suggested are more hindered than **2** since the alkyl substituents on the carbon atoms are not "tied back" as in the dispiro system.
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Nuclear Magnetic Resonance Studies of Metal Complexes Using Lanthanide Shift Reagents. Lanthanide Induced Shifts in the Spectra of Oxygen-Donor Ligands Coordinated to Nickel(II)

Sir:

Since the introduction of lanthanide shift reagents (LSR) in 1969,[1] these reagents have been widely used to simplify the NMR spectra of organic compounds and examples of their use with organometallic compounds have also recently appeared.[2] We now report the successful use of these reagents to induce shifts in the spectra of coordinated ligands in coordination complexes containing oxygen donors. The effect of added shift reagent on the ^1H NMR spectra of a range of diamagnetic nickel complexes of type I has been studied.

The spectrum of *N,N'*-ethylenebis(acetylacetonato)nickel(II) (1, R = CH_3) in deuteriochloroform has been previously described[3] and contains single peaks (δ values) at 1.87 ($-CH_3$), 3.07 ($-CH_2-$), and 4.89 (=CH-) ppm. On successive additions of $Eu(fod)_3$ or $Pr(fod)_3$ to this compound, the proton resonance shifts illustrated in Figure 1 are observed.

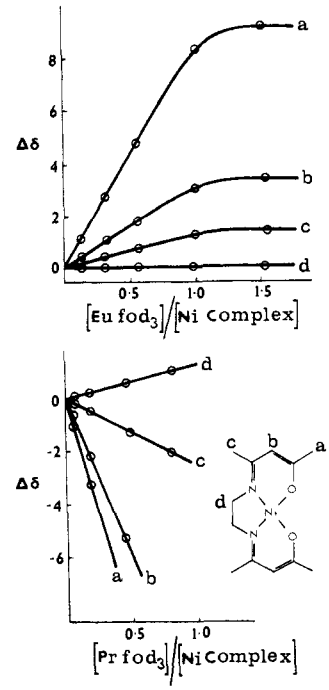
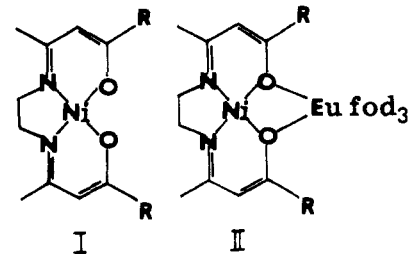


Figure 1. Comparison of the relative chemical shifts ($\Delta\delta$) induced by $Eu(fod)_3$ and $Pr(fod)_3$ in the NMR spectrum of (1, R = CH_3).



As is usually the case with organic compounds, $Eu(fod)_3$ and $Pr(fod)_3$ cause a particular proton resonance to shift in opposite directions. The relative orders of the shifts in Figure 1 are in accord with the LSR interacting with the cis oxygen atoms of the nickel complex as shown by II; however, the possibility that the interaction is monodentate in nature and is associated with a rapid equilibrium between oxygen donor sites on the nickel complex cannot be dismissed on the present evidence. Nevertheless, the ability of europium and praseodymium to expand their coordination numbers from six to eight has been well documented,[4] and the electron lone pairs associated with such cis oxygen donors in related complexes have been shown to be capable of coordinating simultaneously to a second metal ion.[5] Examples of difunctional organic molecules acting as bidentate ligands toward LSR's are also known.[6,7]

It is pertinent that both $Eu(fod)_3$ and $Pr(fod)_3$ have been shown to self-associate (in CCl_4) via bridging β-diketone oxygen donors in a manner which appears analogous to the interactions reported here.[8]

Although a general trend of diminution of shift with distance from LSR is apparent (Figure 1), clearly a detailed analysis of the magnitude of the shifts associated with bidentate systems of the present type is inappropriate in terms of the McConnell-Robertson equation.[7]

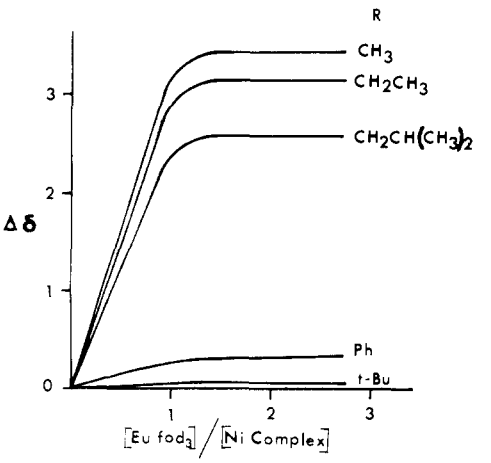


Figure 2. Comparison of the relative chemical shifts of the central proton of the O–N donor chelate rings with change of R for complexes of type I on addition of $Eu(fod)_3$.

Further studies involving complexes of type I in which R becomes successively more bulky also confirm attack of the LSR at the oxygen donors. As the size of R increases, the attachment of the LSR becomes hindered and the magnitude of the shifts of respective resonances decreases for a given LSR:complex ratio (see Figure 2).

Since the limiting shifts (under conditions of excess LSR) also decrease as R becomes more bulky (Figure 2), this implies that there is a change in the geometry of the complex-LSR adduct with change of R. Undoubtedly such a variation will involve a lengthening of the complex-LSR distance as R becomes more bulky.

Although a change of alkyl substituent will also result in concomitant electronic changes which may also influence adduct formation, it seems clear that the considerable differences observed between, for example, the isobutyl and *tert*-butyl derivatives, occur mainly because of the different steric properties of these groups. While this is very likely the case for the series of alkyl derivatives, both steric and electronic effects could well be significant in the phenyl-substituted complex.

To investigate the influence of electronic factors, the complex with R = CF_3 was prepared since this relatively small group should withdraw electron density from the conjugated chelate ring and reduce the capacity of the oxygen donors to coordinate simultaneously to the LSR. Accordingly, no evidence for adduct formation was observed on addition of $Eu(fod)_3$ or $Pr(fod)_3$ to this complex in deuteriochloroform. The disulfur analog[9] of (I, R = CH_3) is also unaffected by either of the above shift reagents and this very likely is the result of electronic effects; the sulfur atoms being softer than oxygen will tend to back-donate electron density into the π-system of the chelate ring rather than to the respective lanthanide ions which, in any case, are known to prefer hard donor atoms.[10]

A range of studies involving the use of LSR's (including chiral reagents) for conformational and other studies in related complexes will be reported soon.

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Synthesis and Reactivity of α-Cyanoenamines. A Novel General Method for Preparing α-Diketones from Amides

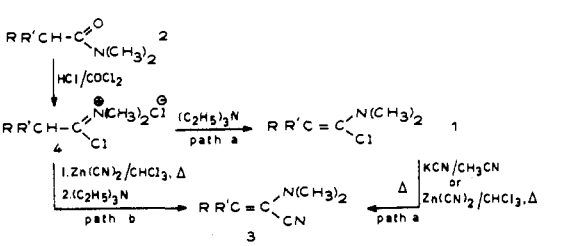
Sir:

We wish to report the utility of α-cyanoenamines as a hitherto unrecognized class of readily available and reactive synthetic intermediates which allow, inter alia, for a versatile and efficient method of synthesis of α-diketones.

The choice of a starting material for the synthesis of α-cyanoenamines has been dictated by our recent studies[1] on α-chloroenamines, a class of reagents readily available from carboxamides.

Indeed α-chloroenamines which already embody most of the structural features of α-cyanoenamines react as keteniminium chlorides and are therefore capable of undergoing nucleophilic substitution with cyanide ion. Thus 1-chloro-*N,N*-2-trimethylpropenylamine (**1a**) readily prepared[1] from *N,N*-dimethylisobutyramide (**2a**) was treated for 40 hr with 1.1 equiv of dry potassium cyanide in refluxing acetonitrile to give 1-cyano-*N,N*-2-trimethylpropenylamine (**3a**) (80% yield, bp 167°, $\nu_{C\equiv N}$ 2205 cm^{-1}). The substitution reaction worked equally well for the synthesis of **3b** from **1b** (80% yield, bp 65° (0.3 Torr), $\nu_{C\equiv N}$ 2200 cm^{-1}). However, replacement of chloride by cyanide in the less electrophilic 1,2-dichloro-*N,N*-dimethylpropenylamine (**1c**) required the presence of a Lewis acid catalyst. Zinc cyanide in refluxing chloroform worked satisfactorily and gave **3c** in 60% yield (purified by GLPC, $\nu_{C\equiv N}$ 2200 cm^{-1}). This procedure (Scheme I, path a) could not be applied to the synthesis of α-cyanoenamines derived from monosubstituted acetamides **2d,e** since the α-chloroenamines **1d,e** are more difficult to prepare and easily undergo thermal or base-catalyzed dehydrochlorination. However, when the di-

Scheme I



a, R = R' = CH_3
b, R = C_2H_5; R' = C_6H_5
c, R = CH_3; R' = Cl
d, R = CH_3; R' = H
e, R = C_6H_5; R' = H