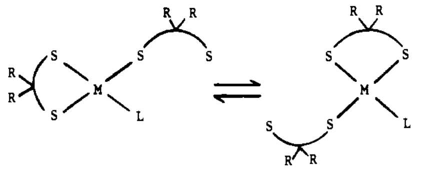
^{77}Se NMR Studies. 2. Intramolecular Rearrangements of the Monophosphine Adduct of Bis(diisobutyldiselenocarbamato)platinum(II), $Pt(Se_2CN$-*i*-$Bu_2)_2PR_3$ ($R = C_2H_5$ and C_6H_5). An Unusual Intensity Distribution of the Satellites Associated with ^{77}Se Coupling in the ^{31}P NMR Spectrum

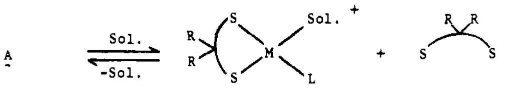
Sir:

The NMR spectra of phosphine adducts of 1,1-dithiolates, $M(S\text{-}S)_2L$, where M = Ni(II), Pd(II), or Pt(II), S-S = $S_2PR_2^-$, $S_2P(OR)_2^-$, $S_2CNR_2^-$, S_2COR^-, or $S_2PF_2^-$ (R = CH_3, C_2H_5, or C_6H_5) and L = a tertiary phosphine, generally show a temperature-dependent behavior.[1-7] This dynamic behavior has been variously interpreted to imply the existence of intramolecular (eq 1) and/or intermolecular (eq 2) rearrangements of the ligands which occur with rates on the NMR time scale. Either process, if rapid, can lead to complete magnetic equivalence of the R groups. Solid-state X-ray structures of the Pd(II)[2b] and Pt(II)[4] complexes consistently show four-coordinate, planar MS_3P geometries about the metal ions. However, with at least one Ni(II) complex, $Ni[S_2P(OC_2H_5)_2]_2P(C_6H_5)_3$, a five-coordinate MS_4P geometry is observed.[7] A five-coordinate species undergoing rapid intramolecular rearrangement without metal-ligand bond rupture (eq 3) also fits much of the NMR data associated with the R groups.

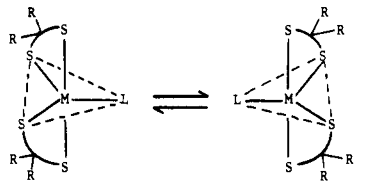


(1)

A



(2)



(3)

Restricted rotation[4,8] about the C$\overset{\cdots}{-}$N bond ($E_a \sim$ 60-95 kJ/mol) adds further complications to the interpretation of ^{1}H or ^{13}C NMR data for the dithiocarbamates, $M(S_2CNR_2)_n$. With the development of high resolution ^{77}Se NMR ($I = \frac{1}{2}$, 7.58% natural abundance),[9] it was appropriate to examine the rearrangement properties of the phosphine adducts of the selenium analogues of the above complexes, creating a situation in which all nuclei in the coordination sphere are NMR active (^{195}Pt, $I = \frac{1}{2}$, 33% natural abundance; ^{31}P, $I = \frac{1}{2}$, 100% natural abundance). We chose $Pt(Se_2CN$-*i*-$Bu_2)_2PR_3$, where R = C_2H_5 or C_6H_5, for this study. *In this complex, it is possible to show conclusively that the lowest energy process producing NMR equivalent chalcogenide ligands is intramolecular.*

^{77}Se NMR studies (Varian XL-100 spectrometer with Gyrocode observe operating at 19.08 MHz) of the title compound (I, L = $P(C_2H_5)_3$), formed by mixing $Pt(Se_2CN$-*i*-$Bu_2)_2$ (II) with the phosphine in a 1:1 molar ratio in a solvent which is a mixture (1:4 volume ratio) of $CDCl_3$ (Norell, refluxed 6 h over P_4O_{10} and distilled) and CHF_2Cl (Freon-22, Matheson, passed through Drierite) or in $CDCl_3$ and $CFCl_3$ (Freon-11, Matheson, refluxed 3 h over P_4O_{10} and distilled) in a 1:1 volume ratio, show at 30 °C a sharp singlet due to II (established by comparing its position with a sample containing no phosphine) and a broad peak ($\Delta\nu_{1/2} \sim$ 160 Hz) ~150 ppm downfield from II, which is associated with the monophosphine adduct. Thus, all four Se nuclei are magnetically equivalent. Using triphenylphosphine, the $^{31}P\{^1H\}$ spectrum indicates phosphine exchange (eq 4) above −20 °C. Phosphine exchange also can produce NMR equivalent R groups.

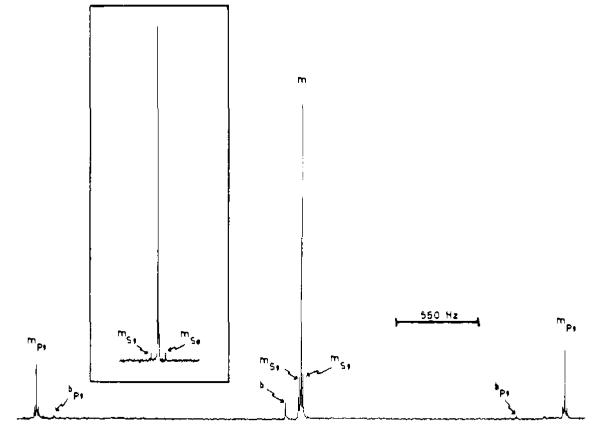
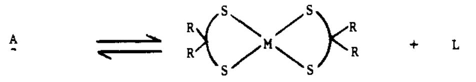


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $Pt(Se_2CN$-*i*-$Bu_2)_2PEt_3$ in $CDCl_3/CFCl_3$ (1:1). Some bisphosphine adduct impurity is indicated by b's (see text). Inset shows the $^{31}P\{^1H\}$ NMR spectrum of $Pt(Se_2CN\cdot i$-$Bu_2)PPh_3Cl$ illustrating the intensities of the ^{77}Se satellites arising from coupling to one Se (^{195}Pt satellites are not shown).[13]



(4)

At −102 °C, the ^{77}Se NMR spectrum shows II, $Pt[(Se_2CN$-*i*-$Bu_2)(PPh_3)_2]^+$, Se_2CN-*i*-Bu_2^-, and four peaks due to I. Identities of the first three species were confirmed by comparison with the spectra of authentic samples. Although ^{195}Pt-^{77}Se couplings could not be observed with certainty owing to the poor signal to noise quality of the spectra, the highest field peak is clearly resolved as a doublet with $^2J_{Se\text{-}P} \sim$ 90 Hz. The $^{31}P\{^1H\}$ NMR spectrum at −93 °C also shows $^2J_{P\text{-}Se}$ = 89 Hz. This high-field peak is assigned to the Se trans to L. Other peak positions are consistent with observations made previously.[9]

The $^{31}P\{^1H\}$ NMR[12] spectrum at 36 °C, of the title compound (I, L = $P(C_2H_5)_3$), in $CDCl_3$-$CFCl_3$ is shown in Figure 1. The monophosphine adduct gives rise to the set of peaks designated m. The m_{Pt} satellites arise from coupling to ^{195}Pt, $^1J_{Pt\text{-}P}$ = 3528 Hz, while m_{Se}'s are satellites arising from coupling to ^{77}Se ($^2J_{P\text{-}Se}$ = 28 Hz). The peaks designated b are associated with the bisphosphine adduct, $[Pt(Se_2CN$-*i*-$Bu_2)(PPh_3)_2]Se_2CN$-*i*-$Bu_2]$. At this temperature, the relative intensities of the m_{Se} satellites on the central ^{31}P signal average 23-28% of the intensity (by peak height measurement) of the total central lines. With four equivalent Se nuclei coupled to phosphorus, the probablity of one being ^{77}Se is 23.9%. As the temperature is lowered, the center triplet changes very little at first, but, at −56 °C, the ^{77}Se satellites are broadened. At about −65 °C, coalescence is achieved. These peaks then broaden into the base line at about −81 °C until, at −93 °C, two new satellites of low intensity appear ($^2J_{P\text{-}Se}$ = 88 Hz). This low intensity doublet is consistent with the phosphorus being trans to a ^{77}Se nucleus (compare $Pt(Se_2CN$-*i*-$Bu_2)PPh_3Cl$, Figure 1, inset). Throughout the temperature range, the ^{195}Pt satellites remain sharp. The changes of the center peaks with temperature are shown in Figure 2.

Thus, the temperature-dependent NMR spectra of I are entirely consistent with a low temperature structure containing bidentate and unidentate ligands, analogous to structures observed crystallographically for the solids involving sulfur ligands.[2b,4] Only one of four selenium nuclei is strongly coupled

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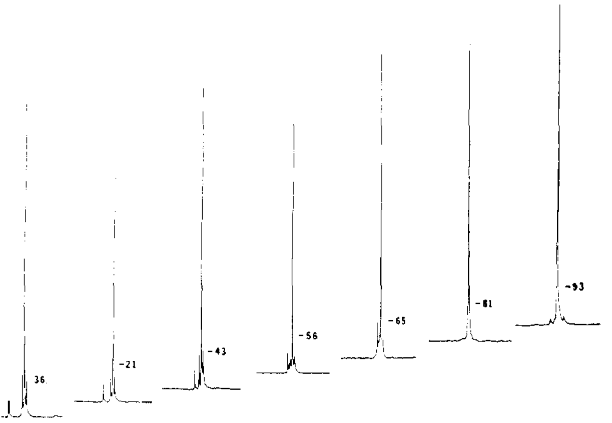

Figure 2. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of Pt(Se_2CN-i-$Bu_2)_2PEt_3$ in $CDCl_3/CFCl_3$ (1:1). The small singlet is bisphosphine adduct impurity. ^{195}Pt satellites are not shown.

to the phosphorus. Since 7.58% of the selenium is NMR active, the total satellite intensity on the $^{31}P\{^1H\}$ signal is ~7.6%. At higher temperatures, but below temperatures which indicate loss of platinum to phosphorus coupling, the ^{77}Se satellite intensities on the $^{31}P\{^1H\}$ spectrum require the four selenium nuclei to appear coupled to the phosphorus with $^2J_{P\text{-}Se}$ ~25% of the low temperature value. (The trans $^2J_{P\text{-}Se} = 88$ Hz and the two cis $^2J_{P\text{-}Se} \sim 5\text{-}10$ Hz,[9] while, for the dangling Se, $^4J_{P\text{-}Se} = 0$ Hz.)[14] The high intensity satellite doublet, $^2J_{P\text{-}Se} = 28$ Hz, results since the percentage of molecules with two or more ^{77}Se on the same molecule is negligible. Intermolecular exchange, which happens at high temperatures, would lead to the complete loss of Pt-P and P-Se couplings. A similar intensity enhancement associated with intramolecular rearrangement was observed by Faller et al.[10] in $(\pi\text{-}C_5H_5)\text{-}W(H)(CO)_3$.

Finally, it is to be noted that all four nonequivalent Se atoms become equivalent at higher temperatures without the detection of a two by two equivalence as expected for a static trigonal bipyramid species (eq 3). Hence, the activation energy to the formation of the five-coordinate intermediate or transition state required in an intramolecular rearrangement is larger than the barrier to the intramolecular five-coordinate rearrangement not involving bond rupture (such as the Berry pseudorotation[11]). In the absence of a five-coordinate pseudorotating intermediate a preferential loss of the ligand trans to phosphorus is expected. Since this also should lead to a two by two equivalence of the Se nuclei, the NMR data is best interpreted by assuming the existence of a rapidly rearranging five-coordinate intermediate along the pathway to chalcogenide ligand interchange.

Acknowledgments. We thank the National Science Foundation, Grant CHE 76-18709, for support of these studies and Professors J. Faller (Yale) and R. Bryant (Minnesota) for helpful comments prior to publication.

References and Notes

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(12) A pulse width corresponding to a flip angle of ~36° was used with a delay time of 1.3 s between pulses. T_1 measurements $(90\text{-}\tau\text{-}180)_n$ of I (L = $P(C_2H_5)_3$) at ~35 °C showed that, within experimental error, the T_1 of the ^{77}Se satellites (2.6 s) is the same as the T_1 of the major peak (2.8 s).
(13) The cis $^2J_{P\text{-}Se}$ of I at low temperature is apparently quite small since the satellites corresponding to such coupling could not be resolved from the major center peak, although some broadening (Figure 2) is noticed in the peak base at low temperatures. In $Pt(Se_2CNEt_2)PPh_3Cl$ the cis $^2J_{P\text{-}Se}$ is 10 Hz.[9] The corresponding satellites are barely observable in the inset of Figure 1.
(14) All $^2J_{P\text{-}Se}$ coupling constants are assumed to have the same sign.

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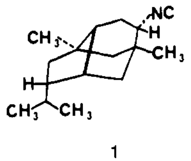
Received October 13, 1978

Total Synthesis of the Racemate of the Sesquiterpenoid Marine Allomone 9-Isocyanopupukeanane

Sir:

The recent report[1] that a sponge (*Hymeniacidon sp.*) produces and transfers to the nudibranch *Phyllidia varicosa* the allomone 9-isocyanopupukeanane (formulated as **1**, or the mirror image)[2] has added a new member to the small but intriguing class of naturally synthesized isocyanides. In addition, it has subsequently been discovered that 2-isocyanopupukeanane (**2**) occurs admixed with **1** or, even exclusively, in individuals of the same species.[3] This communication describes a simple total synthesis of (±)-9-isocyanopupukeanane (**1**) by a route involving a bifunctional *cis*-hydrindan derivative which is also suitable as an intermediate for the synthesis of **2**.[4]

The hydrindanone **3**,[5] mp 64-65 °C, was readily prepared from methyl 3-(4-methoxy-3-methylphenyl)propenate, mp 72-73 °C,[6] in 80% overall yield by conjugate addition of isopropylmagnesium chloride-cuprous phenylmercaptide reagent in dry tetrahydrofuran (THF) at −15 °C for 40 min followed by isolation and cyclization of the resulting 3-isopropyl-3-



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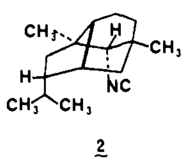

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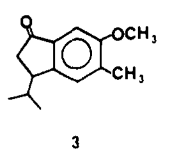

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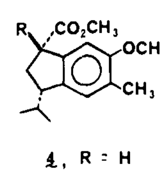
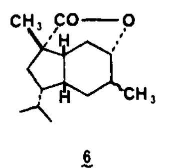


4, R = H
5, R = CH_3



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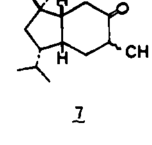

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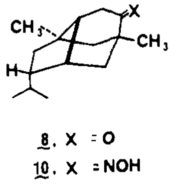
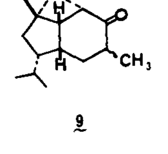


8, X = O
10, X = NOH



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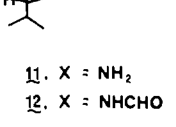
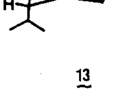


11, X = NH_2
12, X = NHCHO



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