the first clear-cut evidence for counterion control during nondeaminative solvolyses.

(9) There is some doubt (Table II and note 9 of ref 3) as to which of two signals represent C_4 and C_8 (m_c and m_d) in 2-brendyl formate and acetate; further, the C_5 and C_8 signals (m_c and m_d) for 4-brexyl formate were poorly resolved.

(10) The method used involved use of the "area thorem" of J. E. Hearon, and was described by B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4332 (1956).

(11) Calculation of the isotope effects using Charts I and II and eq 1–4 from the data (ref 2, Table I) for the solvolysis of *β-syn*-7-norbornenyl-*α*-d_2 and -*β*-d_2 brosylates gives additional confidence in the validity of the schemes presented here. For the formolysis of 1-α,α-d_2, $m_a = 0.45$, $m_b + m_c = 0.36$, and $m_d = 0.19$. Assuming $m_b = m_c$ and knowing that $k_H'/k_H = 4.18$ from the ^{13}C data, $k_H'/k_D' = 1.67$. In like manner, for the formolysis of 1-β,β-d_2, $m_a = 0.56$, $m_b + m_c = 0.17$, and $m_d = 0.10$, from which $k_H/k_D = 1.7$, and $k_H'/k_H = 4.1$. Similar consistent results can be obtained from the data for acetolyses.

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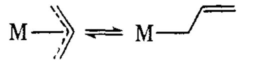
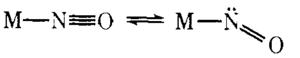
Ligand Dynamics of Ir(NO)(η^3-C_3H_5)$(PPh_3)_2^+$. A Facile Linear-Bent Nitrosyl Equilibrium

Sir:

A key proposal for catalytically active complexes containing allyl and nitrosyl ligands involves a change in bonding mode of the ligands from 3e⁻ to 1e⁻ donors as a means of generating coordinative unsaturation.[1-5] While $\eta^3 \rightleftharpoons \eta^1$ (π-σ) allyl conversion (eq 1) is well documented,[6] evidence for the linear ⇌ bent equilibrium of metal nitrosyls (eq 2) is sparse and, where it exists, ambiguous.[5,7] As part of a study of the relative


(1)


(2)

dynamics of these two ligands, we report the synthesis and solution behavior of $[Ir(NO)(\eta^3\text{-}C_3H_5)L_2]^+$ (L = PPh_3) which exhibits a facile, well-defined linear ⇌ bent nitrosyl equilibrium. The complex also shows allyl fluxionality in a separate process. The X-ray structural characterization of one isomeric form of this cation shows it to be the first example of an η^3-allyl complex containing a bent nitrosyl.

The complex $[Ir(NO)(C_3H_5)L_2]^+$ is prepared as its PF_6^- salt (**1**) by reaction of $[IrCl(NO)L_2](PF_6)$[8] with tetraallyltin at 0 °C in THF, followed by precipitation with Et_2O and recrystallization from CH_2Cl_2/Et_2O, to give light-brown needles in 60–70% yield.[9] Repetition of the synthesis using $[IrCl(NO)L_2](BF_4)$, followed by similar isolation techniques, affords the BF_4^- salt hemihydrate (**2**) as red-brown crystals.[10] Both **1** and **2** are air stable as solids and moderately air stable in solution.

Infrared spectra of **1** and **2** in the solid state (KBr pellet) exhibit single nitrosyl stretches but with values differing by 130 cm⁻¹ (ν_{NO} 1763 and 1631 cm⁻¹, respectively). Solutions of either compound in CH_2Cl_2 or CH_3CN at 30 °C show both stretches at equal intensity, however. Cooling of these solutions causes an increase in the intensity of the 1763-cm⁻¹ band with a simultaneous decrease in the 1631-cm⁻¹ stretch. This spectral change is reversible; repeated cooling and warming of the same sample give identical results. The sum of the absorbances for these two bands is constant as a function of temperature within experimental error.

The existence of two nitrosyl stretches in solutions of $Ir(NO)(C_3H_5)L_2^+$, together with our ability to isolate two separate species, each containing only one ν_{NO} in the solid state, leads to the conclusion that two isomeric forms of the cation exist which are in equilibrium in solution. The constancy of the sum of the ν_{NO} absorbances over the temperature range ~−50 to +30 °C lends support to this notion.

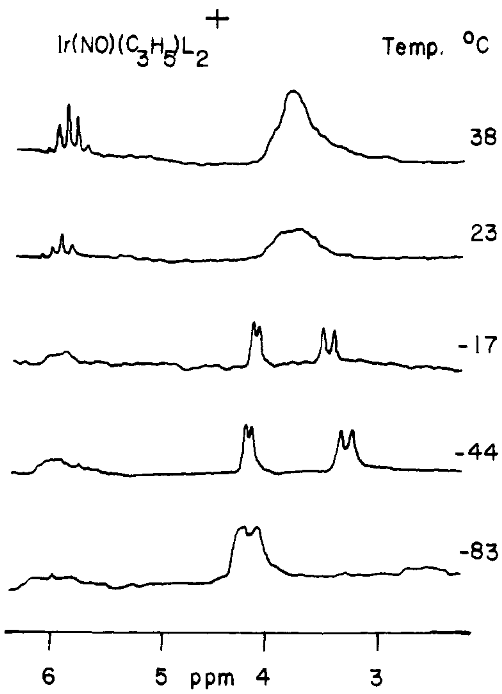
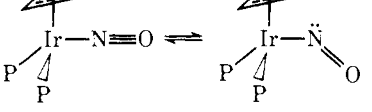


Figure 1. Allyl ¹H NMR spectra of $[Ir(NO)(C_3H_5)(PPh_3)_2]^+$ as a function of temperature in acetone-d_6.

The ¹H NMR spectra of **1** and **2** in acetone-d_6 are identical and also provide evidence of dynamic behavior as the temperature is varied. Representative spectra are shown in Figure 1. At 37 °C the spectrum consists of a quintet at δ 5.8 whose spacing is 9 Hz and a broad resonance at 3.8 (integrated ratio 1:4). Cooling of the sample to −44 °C leads to a single allyl pattern which unambiguously characterizes the allyl bonding mode as trihapto: central proton (A), δ 6.0 (m); syn protons (B), 4.24 (d); anti protons (C), 3.36 (d); integrated ratio A:B:C, 1:2:2; $J_{AB} = 7$, $J_{AC} = 11$ Hz. At even lower temperatures (−83 °C), a new pattern emerges which is not readily interpretable. It does indicate that an additional dynamic process is occurring at lower temperatures, but, in light of the spectra at −44 and −17 °C, syn-anti exchange can not be involved.

From both the IR and NMR spectra of $Ir(NO)(C_3H_5)L_2^+$ it is clear that several dynamic processes are occurring in solution. The most intriguing of these is the facile interconversion of the two nitrosyls. The fact that both nitrosyl stretches are observed in the temperature range −50-0 °C in which only η^3 coordination of the allyl exists leads to the conclusion that the two isomers are not related by $\eta^3 \rightleftharpoons \eta^1$ allyl fluxionality. The equilibration of the isomers is, however, rapid on the NMR time scale. We therefore propose the interconversion of the two isomers to be a simple bending and straightening of the Ir-NO unit as shown in eq 3.


1 **2**
(3)

The higher value of ν_{NO} for isomer **1** is consistent only with a linearly coordinated nitrosyl, and the structure of **1** is thus assigned as shown in eq 3 in analogy to the X-ray-determined structure of the 18e⁻ complex $Ru(NO)(\eta^3\text{-}C_3H_5)L_2$ reported

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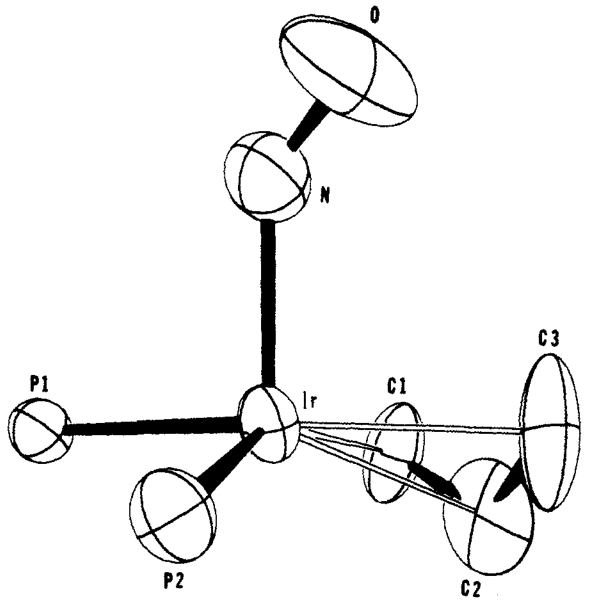


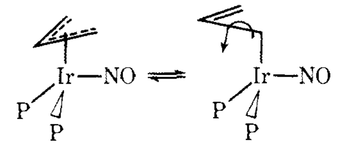
Figure 2. Perspective view of the inner coordination sphere of [Ir(NO)(η^3-C_3H_5)(PPh_3)$_2$](BF_4)·½H_2O. Important distances and angles follow: Ir-P(1), 2.338 (3), Ir-P(2), 2.363 (3), Ir-C(1), 2.21 (1), Ir-C(2), 2.17 (1), Ir-C(3), 2.27 (1), Ir-N, 1.95 (1), N-O, 1.11 (1), C(1)-C(2), 1.34 (2), C(2)-C(3), 1.50 (2) Å; Ir-N-O, 129 (1), C(1)-C(2)-C(3), 121 (1), P(1)-Ir-P(2), 102.9 (1), P(1)-Ir-N, 95.0 (3), P(2)-Ir-N, 96.3 (3), P(1)-Ir-C(1), 94.6 (4), P(2)-Ir-C(3), 93.6 (3), N-Ir-C(1), 89.7 (6), N-Ir-C(3), 105.1 (5)°.

previously.[11] In the case of **2**, the ν_{NO} value of 1631 cm^{-1} falls within the range of ambiguity (1720–1600 cm^{-1}) for the assignment of nitrosyl bonding mode,[12] and a structure determination was therefore deemed necessary.

Crystals of **2** belong to the monoclinic space group $I2/c$ in a cell of dimensions a = 27.79 (3), b = 13.57 (1), c = 20.70 (2) Å; β = 104.84 (3)°; Z = 8. The structure was solved by standard heavy-atom methods and refined by least-squares procedures to final agreement factors R and R' of 0.055 and 0.077 for 5135 reflections having $F_o \geq 3\sigma(F_o)$ and 168 variables.[13] Tables of final structural parameters and intramolecular distances and angles are available as supplementary material (see paragraph at the end of this article).

A perspective view of the inner coordination geometry of cation **2** is shown in Figure 2 with important distances and angles given in the caption. The nitrosyl is clearly bonded in a bent manner (Ir-N-O, 129 (1)°), while the allyl is maintained in a trihapto bonding mode. As such, this is the first crystallographic evidence for a bent nitrosyl and a π-allyl at the same metal center.[11] A description of the coordination geometry of **2**, a 16e$^-$ system, depends in large measure on whether π-allyl bonding is viewed as monodentate or bidentate. The former leads to a distorted tetrahedron for which there exists recent precedent in the Ru(0) complex Ru(styrene)$_2$L$_2$,[14] while the latter leads to a square pyramidal model with a bent nitrosyl in the apical position, which is consistent with all previously reported five-coordinate structures of bent nitrosyl systems.[15] Based on the structural evidence for **2** and the Ru linear nitrosyl analogue[11a] of **1**, a modification to eq 3 has been suggested by one reviewer in which the allyl group rotates about the metal-allyl center of mass vector as the nitrosyl bends in a coupled motion. Such a rotation does not involve syn-anti exchange in accord with the evidence, and therefore cannot be ruled out. We believe, however, that this type of allyl rotation may be occurring separately and independently, and account for the changing NMR spectrum below −50 °C.

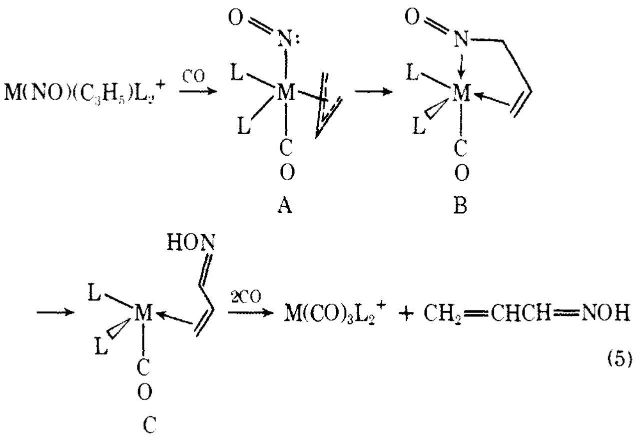
In addition to equilibrium 3, another facile process is important at higher temperatures involving equilibration of the *syn*- and *anti*-allyl protons, most probably via an $\eta^3 \rightleftharpoons \eta^1$ mechanism as shown in eq 1. From temperature-dependent NMR studies we estimate an enthalpy of activation, $\Delta H^{\ddagger}$, of 5 ± 1 kcal/mol for this process. Whether syn–anti exchange proceeds from isomer **1** or **2** remains to be established; however it seems reasonable that, in view of the preponderance of 18e$^-$ $\rightleftharpoons$ 16e$^-$ processes, the interconversion proceeds from **1** according to eq 4.



(4)

The NMR spectrum at −83 °C, which differs from that at −44 °C, may be due to a slowing of equilibrium 1, thus allowing observation of the allyl ligand in its two different chemical environments, or to the existence of two conformers of the same isomer differing only in the orientation of the allyl with respect to the nitrosyl ligand.[16] Evaluation of this dynamic process will require better low temperature limiting spectra.

In addition to the unique ligand dynamics of the iridium cation, we have found that this complex, as well as the isoelectronic species [Rh(NO)(η^3-C_3H_5)L$_2$]$^+$ (**3**),[17] prepared by reacting [RhCl(NO)(CH_3CN)L$_2$]$^+$ [18] with (C_3H_5)$_4$Sn at 0 °C, reacts rapidly with CO to give acrolein oxime[19] and the corresponding M(CO)$_3$L$_2^+$ complex, probably via an intramolecular coupling process as shown in eq 5.



(5)

Precedent for intermediate A has been established by the detection of Ru(NO)(CO)(η^3-C_3H_5)L$_2$ which has been shown to possess a necessarily bent nitrosyl.[11] Coupling of the nucleophilic bent nitrosyl with the potentially electrophilic η^3-allyl ligand then gives a nitrosopropene species, B, which tautomerizes to the more stable oxime. The isolation of an acrolein oxime complex of Ni from the reaction of NO(g) with [Ni(η^3-C_3H_5)Br]$_2$ establishes a precedent for C.[20]

The electrophilic nature of the allyl ligands in these complexes is further evidenced by their reactions with PPh$_3$ and pyridine to give the corresponding allylphosphonium and allylpyridinium salts and neutral nitrosyl phosphine complexes in quantitative yield.[21]

These studies thus provide a direct internal comparison of the dynamic behavior of nitrosyl and allyl ligands, and demonstrate the feasibility of their coupling to give oxime when their bonding modes and reactivity patterns differ.

Acknowledgments. We thank the National Science Foundation (Grant CHE 76-17440), for support of this research, and Matthey Bishop Co., Inc., for a generous loan of transition metal salts.

Supplementary Material Available: Tables of final structural parameters and intramolecular distances and angles with estimated standard deviations (4 pages). Ordering information is given on any current masthead page.

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(9) Anal. Calcd for $C_{39}H_{35}F_6IrNOP_3$: C, 50.21; H, 3.79; N, 1.50; P, 9.96. Found: C, 50.34; H, 3.90; N, 1.60; P, 9.79. Elemental analyses performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(10) Anal. Calcd for $C_{39}H_{35}BF_4IrNOP_2 \cdot \frac{1}{2}H_2O$: C, 53.01; H, 4.11; N, 1.58. Found: C, 53.02; H, 4.40; N, 1.41. The crystals were grown in an open flask stored in a refrigerator. The occurrence of a hydrate, as judged from the structure determination, is therefore not surprising.

(11) (a) M. W. Schoonover and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 8371 (1977). (b) Both A and $Ru(NO)(CO)(\eta^3\text{-}C_3H_5)L_2$ characterized previously[11a] are proposed to have trigonal–bipyramidal structures in which the η^3-allyl ligand occupies only a single coordination site. If the $\eta^3\text{-}C_3H_5$ ligand is assumed to take up two coordination sites, then A and $Ru(NO)(CO)(\eta^3\text{-}C_3H_5)L_2$ are both distorted octahedral structures. Both formalisms regarding η^3-allyl coordination have been invoked. The cis disposition of the PPh_3 ligands in A is based on the X-ray structure of **2**, while the trans disposition in $Ru(NO)(CO)(\eta^3\text{-}C_3H_5)L_2$ was proposed based on the tendency of PPh_3 to be mutually trans. The relative disposition of the PPh_3 ligands does not affect our proposal regarding the chemical reactivity of these coordinatively saturated allyl nitrosyl species.

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(13) Structural details will be published separately.

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(16) See, for example, A. Davison and W. C. Rode, *Inorg. Chem.*, **6**, 2124 (1967); J. D. Smith and J. D. Oliver, *ibid.*, **17**, 2585 (1978).

(17) Anal. Calcd for $C_{39}H_{35}ClF_6NOP_3Rh$: C, 53.55; H, 4.10; N, 1.58; P, 10.48. Found: C, 53.00; H, 4.30; N, 1.67; P, 10.10. Allyl spectra: δ 5.84 (A, m), 4.44 (B, d), 3.20 (C, d) ($J_{AB} = 7$, $J_{AC} = 14$ Hz); ν_{NO}(KBr) 1658 cm^{-1}.

(18) N. G. Connelly, P. T. Dragget, M. Green, and T. A. Kuc, *J. Chem. Soc., Dalton Trans.*, 70 (1977).

(19) Identified by NMR and GC/MS comparison with those of an authentic sample prepared independently (cf. N. G. Koral'nik et al., *Zh. Prikl. Khim.*, **36**, 1627 (1963); *Chem. Abstr.*, **59**, 15171a (1953)). ^{1}H NMR: terminal protons C and D, 5.4, 5.5 (2d); proton B, 6.2–6.6 (m); proton A, 7.6 (d) ($J_{AB} = 9$, $J_{BC} = 8$, $J_{BD} = 18$ Hz). The hydroxyl proton resonance was too broad to detect. No additional organic products such as hexadienes were found. The reaction to give oxime appears quantitative but the instability of the oxime product toward polymerization makes accurate measurement difficult. See also ref 20 for nitrosyl–allyl coupling.

(20) (a) R. A. Clement, U.S. Patent 3 652 620 (March 1972); (b) R. A. Clement, U. Klabunde, and G. W. Parshall, *J. Mol. Catal.*, **4**, 87 (1978).

(21) Reaction of 0.107 mmol of **1** with 0.214 mmol of PPh_3 in CH_3CN yielded $Ir(NO)L_3$ (75% isolated) and $C_3H_5PPh_3{}^+P_6{}^-$ (65%). Reaction of 0.135 mmol of **3** with 0.270 mmol of PPh_3 gave $Rh(NO)L_3$ (81%) and $C_3H_5PPh_3{}^+BF_4{}^-$ (85%). Products were characterized by comparisons with authentic samples. Reactions with pyridine and these complexes in CH_3CN yielded 30–40% $M(NO)L_3$ as a precipitate. Quantitative conversion of allyl to $[C_3H_5\text{–}NC_5H_5]^+$ was observed via ^{1}H NMR.

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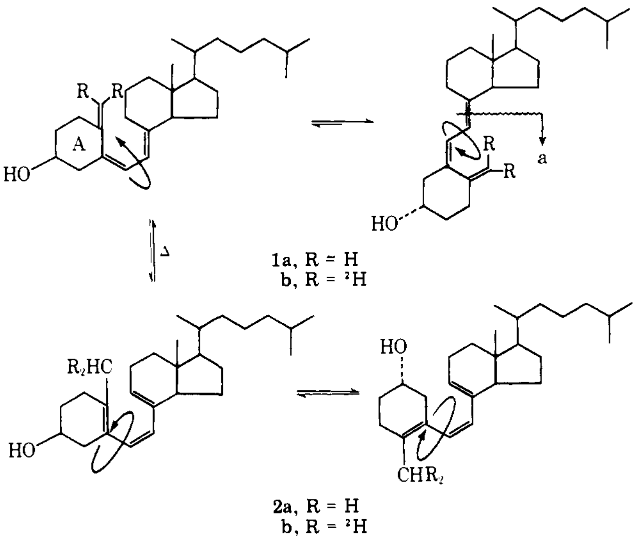
Use of ^{2}H NMR and Mass Spectrometry for the Investigation of the Vitamin D_3–Previtamin D_3 Equilibrium

Sir:

Vitamin D_3 is formed biogenetically from 7-dehydrocholesterol by irradiation followed by isomerization of the resulting previtamin D_3.[1] Establishment of the intramolecular and uncatalyzed nature of the isomerization[2] led to the postulate that it occurs by antrafacial, sigmatropic 1,7-hydrogen migration.[3] This migration may take place from two diastereomeric conformations of the *cis*-1,3,5-trienes, but, as expected for a biological process, only one should be preferred. However, Akhtar and Gibbons[4] suggested the absence of such preference on thermal equilibration of previtamin, claiming tritium scrambling between the 19, 9α, and 9β positions of the vitamin after 2-h heating of the C-19-tritium-labeled previtamin.

Scheme I. Thermal equilibrium previtamin D–vitamin D



1a, R = H
b, R = ^{2}H

2a, R = H
b, R = ^{2}H

We prepared [19,19-^{2}H]vitamin D_3 (**1b**) by reacting the dimethylene ketone analogue of vitamin D_3 with triphenylphosphine [^{2}H]methylene.[5] The integration of the two signals of C-19 protons (at 4.7 and 4.9 ppm)[6] indicated that **1b** was ~80% d_2-isotopically pure. Heating of **1b** in isooctane at 80 °C for 2 h results in a 80:20 equilibrium mixture of vitamin D_3 (**1**) and previtamin D_3 (**2**)[2] (Scheme I). Surprisingly we have observed that the ^{1}H NMR spectra of the vitamin before and after thermal equilibration were practically identical. In addition, the spectrum of the isolated previtamin was consistent with the structure in which all the deuterium was at C-19, the signal intensity of the vinylic proton at C-9 (at 5.50 ppm) corresponding to a full proton. It appears that the vitamin D_3-previtamin D_3 equilibrium was attained by 1,7-protium migration rather than by deuterium migration.

Deuterium migration from C-19 to C-9 could only be detected after prolonged heating. Thus, after 14 h at 80 °C, the ^{1}H NMR of **1b** showed an increase of ~40% in the intensity of the signals due to protons at C-19 and a decreased intensity of the signal at 2.7 ppm which was assigned by Wing et al.[6b,7] to the 9β proton. However, it was difficult to decide whether changes occurred in the 9α proton signals (centered at 1.68 ppm[7]) since it was overlapped by other protons.[8] The ^{1}H NMR spectrum of previtamin D_3 (**2b**) also changed on prolonged heating, the signal intensity of the C-9 vinylic proton decreasing considerably.

The intramolecular isotope exchange rate could be monitored by mass spectrometry of **1b**, based on the finding that the characteristic abundant ion a[5,9] which includes ring A, C-6, and C-7 of the molecular ion contained the major part of its original label (Table I). We have heated the labeled vitamin D_3 (**1b**) for different periods of time and have determined the deuterium distribution in the molecular ion (*m/e* 384–386), and in the ion a (*m/e* 136–138) regions.[10,11] Table I shows that, while the isotopic composition of the molecular ion of **1b** remains practically unchanged during the 14-h heating, the number of deuterium atoms retained at C-19 decreased gradually. Complete distribution of the deuterium label be-