Table I. Quantum Yields and Triplet Reactivities[a] of 4-Acylpyrimidines

Pyrimidine	Φ_{II}[b]	Φ(Cyclopropanol formation)	Slope $Kq\tau$ (M^{-1})	$1/\tau(10^8)$ s^{-1}
(**1**) 4-Propionyl[c]	—	0.34[e]	75	0.67
(**2**) 4-Butyryl[d]	0.13	0.18	30	1.67
(**3**) 4-Valeryl[d]	0.26	—	4.15	12

[a] In benzene solvent, $Kq = 5 \times 10^9$ M^{-1} s^{-1}. [b] Quantum yield for 4-acetylpyrimidine formation. [c] Originally 0.01 M in ketone. [d] Originally 0.05 M in ketone. [e] In *tert*-butyl alcohol.

abstraction occurs from ketone **1**, that competitive C=N and C=O hydrogen abstraction occurs from ketone **2**, and that C=O hydrogen abstraction predominates from ketone **3**.

The photoreactions of ketones **1**, **2**, and **3** were quenched using 1,3-pentadiene. Quantitative information regarding their respective triplet reactivities was calculated from Stern-Volmer plots[6] and eq 1.

$$\Phi_0/\Phi = 1 + Kq\tau[Q] \qquad (1)$$

The reaction quantum yields and triplet reactivities are summarized in Table I. The data in Table I indicate that the valerylpyrimidine triplets are about seven times more reactive towards intramolecular hydrogen abstraction than the 4-butyrylpyrimidine triplets and that the 4-butyrylpyrimidine triplets are about two and a half times more reactive than the corresponding 4-propionylpyrimidine triplets. However, since about 42% of the triplet reactivity of 4-butyrylpyrimidine (**2**) is due to the C=O chromophore and 58% to the C=N a more accurate estimate of the relative triplet carbonyl reactivity of ketone **3** to **2** (secondary vs. primary hydrogen abstraction) is 17.[7] By analogy, the relative triplet C=N reactivity of ketone **2** to **1** (secondary vs. primary hydrogen abstraction) is found to be only 1.5.[9]

When one compares the reactivities of the C=O and C=N chromophores directly, the C=O and C=N triplets are found to possess about equal reactivity towards primary hydrogen atoms (7.0×10^7 s^{-1} vs. 6.7×10^7 s^{-1}). Towards secondary hydrogens, however, the C=O triplets are found to be 12 times more reactive than the C=N triplets (12×10^8 s^{-1} vs. 0.97×10^8 s^{-1}). The latter indicates why little to no cyclopropanol formation occurs from the photolysis of 4-valerylpyrimidine (**3**).

The observed lack of selectivity of the C=N triplets of 4-acylpyrimidines towards primary vs. secondary hydrogen atom abstraction cannot be unequivocally explained on the basis of our present data. It may indicate that hydrogen abstraction by the C=N chromophore unit is more exothermic and involves a lower activation energy than that of the C=O. Such an explanation has been used to rationalize the low selectivity of certain free radicals towards abstraction of secondary vs. primary hydrogen atoms.[10] The fact that the C=N and C=O triplets exhibit about equal reactivity towards primary hydrogens, however, suggests that additional factors must influence the hydrogen abstraction process.

Triplet ketones have been compared to alkoxy radicals in terms of their selectivity towards C-H bond abstraction.[8] A similar comparison of C=N triplets to amino radicals would be of interest here. Unfortunately the scarcity of available reactivity data[11] on amino radicals does not permit such a comparison at this time.

To our knowledge this work represents the first quantitative estimation of the relative triplet reactivity of a C=O vs. C=N chromophore unit. We are presently investigating the mechanism of the C=N hydrogen abstraction process in greater detail.

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(6) The Stern-Volmer plots were linear out to Φ_0/Φ values of 9, 4, and 2.
(7) The observed carbonyl rate enhancement is in excellent agreement with what has been previously reported for the relative reactivity of carbonyl triplets towards secondary vs. primary hydrogens.[8]
(8) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
(9) The diradical intermediates in the two competing reactions may revert to the ground state of ketone (**2**) with different probabilities. Under such conditions the product ratio from (**2**) would not exactly correspond to the 42/58 rate ratio. However, from the behavior of ketones (**1**) and (**3**) it does appear that the estimation is nearly exact.
(10) (a) W. A. Pryor, "Free Radicals", McGraw Hill, New York, N.Y., 1966, p 154; (b) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
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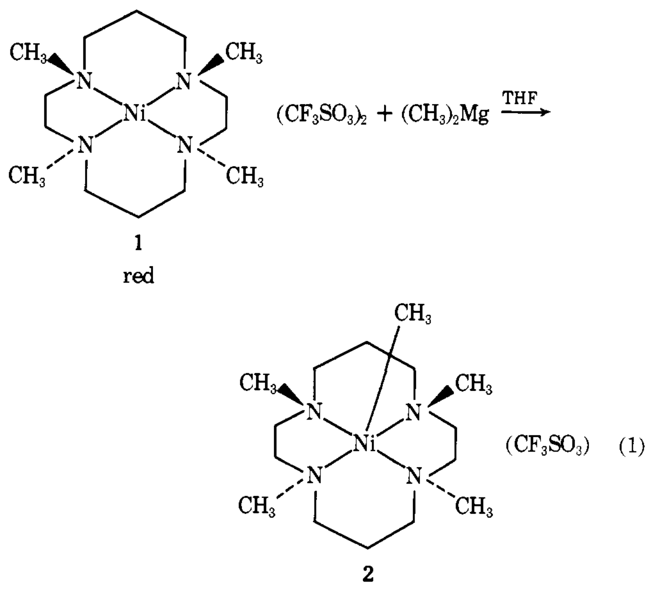
A Paramagnetic, Square-Pyramidal Nickel(II) Alkyl Complex

Sir:

A large number of nickel(II) complexes containing alkyl ligands have been prepared; however, except for one tetrahedral example, these are four- or five-coordinate,[1] diamagnetic compounds.[2] Although it is generally not stated explicitly, high-spin nickel alkyl complexes are expected to be very unstable. We have prepared a square-pyramidal, high-spin nickel(II) alkyl complex, which is stable at room temperature, by alkylation of **1**. The synthesis and properties of this unique compound are the subject of this communication.

Addition of a slight excess of dimethylmagnesium[3] to a suspension of 1 g (1.6 mmol) of **1**[4] in 25 ml of purified THF at room temperature under nitrogen produced an emerald green solution. After dissolution of all of the starting material (about 15 min), the volume of the solution was reduced to 10 ml, and 20 ml of ether was added to yield crystalline **2**. Recrystallization was by dissolution in THF followed by addition of ether. Yield, 0.57 g, 75%. Anal. Calcd for $NiC_{16}H_{35}N_4O_3SF_3$: Ni, 12.24; C, 40.08; H, 7.36; N, 11.69. Found: Ni, 12.32; C, 40.33; H, 7.35; N, 11.70. Green solutions similar to those of the methyl complex were generated using diethyl- or diphenylmagnesium in place of the dimethyl compound but products have not been isolated in pure form.

Reaction of the perchlorate salt of **1** with 1 equiv of lithi-



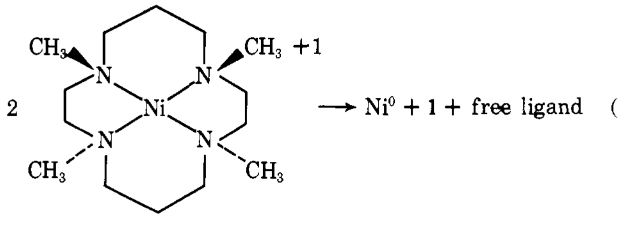
1
red

2
green

um chloride in THF also produced a green solution from which a green chloro complex (**3**) was obtained by a procedure similar to that described above.

Magnetic moments of **2** and **3** were 2.78 and 3.03 μ_B, respectively. Absorption spectra of **2** and **3**,[5] obtained on THF solutions are very similar to those of square-pyramidal nickel(II) complexes prepared from a stereoisomer of **1**.[6] We expect that **2** and **3** also have square-pyramidal structures.

As a solid, **2** was stable for several days at room temperature under nitrogen and it only slowly decomposed when exposed to air. In THF solution, **2** did not decompose appreciably for several hours under nitrogen at room temperature. Decomposition occurred fairly rapidly when the solution was heated. Ni(I) complex (**4**) was identified as a product of the thermal decomposition.[7] Presumably **4** formed by homolysis of the nickel-carbon bond but gaseous products have not been identified. Qualitatively, photolysis did not increase the rate of formation of **4**. Complex **4** is quite unstable and decomposes according to eq 2.[7]



4

The methylato complex (**2**) is very soluble in pyridine, trimethyl phosphite, and water; thermal stability of **2** in the first two solvents is comparable to that in THF. Decomposition occurred in water ($t_{1/2}$ about 15 min), and a basic solution of **1** formed. The rate of decomposition decreased with time and subsequent experiments showed that the rate was lower in basic solution. Addition of H^+ to aqueous solutions of **2** caused rapid evolution of methane (about 1 mol/mole of complex).[8] Chloro complex **3** dissolved in water to give only a red solution of **1**. Although six-coordinate complexes of **1** have been isolated,[4] the complex is four-coordinate in water in the absence of high concentrations of ligand. The contrasting behavior of **2** and **3** is most likely a result of the hydrophobic nature of the axial methyl ligand whereas the coordinated chloride ion is highly solvated by water and thus easily removed from the coordination sphere of the nickel ion.

Other electrophilic reagents besides H^+ reacted with **2**. Green aqueous solutions of **2** instantly turned red upon addition of Hg^{2+}. CH_3Hg^+ and **1** were identified as products.[9] Reactions also occurred with SO_2 and CO_2, forming products containing methyl sulfinate and acetate.[10] No information concerning the mechanism of formation of these products is presently available.

The ground-state electronic structure of high-spin d^8 metal complexes having square-pyramidal geometry is $(d_{xz}, d_{yz})^4 d_{xy}{}^2 d_{z^2} d_{x^2-y^2}$.[11] Consequently all d orbitals that are available for σ bonding are partially occupied and bonding of the methyl group to the nickel ion in **2** must be largely electrostatic. The reactivity of **2** toward electrophilic reagents is ample demonstration of the expected electron-rich nature of the carbon-nickel bond. It is also clear that **2** is stable in nucleophilic solvents and that it has substantial thermal stability both as a solid and in solution. It is doubtful that the stability of the metal-carbon bond is determined in any unique way by the macrocylic tertiary amine ligand although the kinetic stability of **1** and its resistance to strong base are due to the structure of the ligand and the steroechemistry of the complex. We expect that alkyl complexes can be generated from other inert nickel(II) complexes that are not susceptible to competing reactions with the strongly basic alkylating agents required for their formation.

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References and Notes

(1) Five-coordinate examples contain the cyclopentadienyl group and are of the form $[(\eta^5\text{-}C_5H_5)Ni(R)L]$.

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(5) Spectral parameters are: (**2**) 8300 cm^{-1} (ϵ = 14.4), 8850 (15.2), 10 800 (10.7), 14 930 (53.4), 28 370; (**3**) 8060 (2.4), 8630 (2.4), 11 110 (3.0), 12 270 (2.9), 15 660 (11.1), 25 090 (24.7), 30 670 (10.7).

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(7) Complex **4** was also prepared by sodium amalgam reduction of 1 in THF-acetonitrile. It was a pale green material that had an axial ESR spectrum ($g_\parallel$ = 2.306, $g_\perp$ = 2.070; frozen THF-toluene solution at about −196°) which was independent of the method of preparation. On standing in THF **4** decomposed to a black solid (soluble in nitric acid, positive test for nickel with dimethylglyoxime), **1**, which crystallized as the decomposition proceeded and was identified by comparison of its infrared spectrum with that of an authentic sample and free ligand (identified by NMR after it was extracted from evaporated reaction mixtures with chloroform).

(8) Gas collected in a buret over water. Identification was by GLC on a column of Waters Associates *n*-octane/Porasil C, 100–120 mesh.

(9) CH_3Hg^+ was identified by its NMR spectrum, which was obtained on D_2O reaction mixtures (τ 9.02, $J_{Hg^{199}\text{-}CH_3}$ 263 Hz). Starting material crystallized when reaction mixtures were reduced in volume and was identified by infrared spectroscopy.

(10) **2** reacted as a solid with both gaseous and liquid SO_2. Extraction of the reddish products with ethanol yielded blue solutions and a residue. The residue was 1 (by infrared). A blue complex was obtained from the extract whose analysis and infrared spectrum was consistent with a bismethylsulfinate complex of cation **1**. Reactions with CO_2 were done on THF solutions of **2** under 30–40 psi of gas. Greenish oils were obtained, which have not been successfully purified; however, these products showed a strong absorption in the infrared spectrum at 1620 cm^{-1} that is attributed to acetate.

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