${}_2\sigma_s + {}_2\pi_s$ cycloaddition (excited state allowed) followed by nitrogen disengagement which is also excited state allowed (eight electrons, Hückel) or equivalently a reverse ${}_2\sigma_s + {}_2\pi_s + {}_2\sigma_s + {}_2\pi_s$.[13]

Thus, the concept of generating species on photochemical hypersurfaces has again proven of utility in determining photochemical details.[16] In this instance the diradical postulated 8 years ago[5a] has proven a reality.

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(13) As noted earlier by us,[10b] and most recently by Day,[14] the Hückel–Möbius and generalized Woodward–Hoffmann treatments[15] are perfectly analogous, since the number of sign inversions in a pericyclic transition state is simply equal to the number of antara components in the generalized Woodward–Hoffmann rule.

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Oxygenation of the Nitrosyl Ligand in Complexes of Iridium

Sir:

Synthetic and structural studies of metal-nitrosyl complexes have recently attracted considerable attention because of their importance in developing an understanding of reactions of small molecules which play significant roles in living systems or in industrial catalytic reactions. The chemical reactivity of the coordinated nitrosyl ligand depends on its mode of bonding.[1] While many complexes with linear M-N-O bonds and with ν(NO) usually greater than 1850 cm^{-1} react with nucleophiles such as OH^- or N_3^-,[2] certain complexes with bent M–N–O bonds undergo electrophilic attack. These latter sparsely studied reactions include protonation[3] to form the coordinated nitroxyl (HNO) or hydroxylamine ligands and oxidation with nitric oxide[4] or dioxygen. In the presence of bases five-coordinate nitrosyl complexes can be oxygenated to form nitro complexes[5] or mixtures of nitro and nitrato complexes.[6,7] It has been suggested recently that ν(NO) may serve as a useful criterion for predicting whether oxygenation will give MNO_2 or MNO_3 products, namely, that complexes with low ν(NO) (1600-1710 cm^{-1}) give MNO_2 complexes, while complexes with ν(NO) at higher frequencies (1710-1765 cm^{-1}) give MNO_3 complexes.[6] Our observations indicate that ν(NO) is not a useful criterion.

Table I. Selected Infrared Spectral Data[a] (cm^{-1}) for $Ir(PPh_3)_2(CO)ClX(NO)$ and Experimentally Observed Rate Constants for the Reaction $Ir(PPh_3)_2(CO)ClX(NO) + O_2 \rightarrow Ir(PPh_3)_2(CO)ClXNO_3$ at 25°C and Partial Pressure of O_2 at 619 Torr

X	ν(CO)	ν(NO)	$10^3 k_{obsd}$, (sec^{-1})
I	2055	1550	184.
Br	2059, 2040 sh	1560, 1530	40.4
	2020,		
Cl[b,f]	2060, 2040 sh	1560, 1520	8.25
NCS[c]	2055	1545	6.68
NCO[d]	2040	1540	3.42
N_3[e]	2050	1540	1.59

[a] In KBr. [b] Bands in CH_2Cl_2 at 2057, 1535 cm^{-1}. [c] ν(NCS) at 2090 cm^{-1}. [d] ν(NCO) at 2225 cm^{-1}. [e] $\nu(N_3)$ at 2030 cm^{-1}. [f] ν(Ir–Cl) at 307 307 (w) and 200 (vw) cm^{-1}.

We report herein the synthesis of a new class of iridium nitrosyl complexes with NO stretching frequencies in the 1520-1560-cm^{-1} region (among the lowest yet reported for metal nitrosyls) and the oxygenation of these complexes exclusively to nitrato complexes.

The crystal structure of $[Ir(PPh_3)_2(CO)(NO)Cl]BF_4$ (**1**), determined by Ibers and Hodgson,[8] revealed the first example of a metal-nitrosyl complex with a bent M–N–O bond. Rather surprisingly reports on the reactions of **1** have not appeared. Compound **1** (previously reported as an 18-electron complex)[9] was carbonylated to give $[Ir(PPh_3)_2(CO)_2Cl(NO)]BF_4$ (**2**), a 1:1 electrolyte in nitromethane.[10] Compound **2** has ν(CO) at 2070, 2023, and 1980 cm^{-1}, ν(NO) at 1680 cm^{-1}, and $\nu(BF_4)$ at 1060 cm^{-1}.

Addition of solutions of LiCl or HCl in methanol to violet dichloromethane solutions of **1** gave immediate decoloration. Partial evaporation of solvent with a stream of nitrogen led to crystallization of yellow-green $Ir(PPh_3)_2(CO)(NO)Cl_2$. Other coordinating anions X^- added as Li^+, Na^+, K^+, or NH_4^+ salts gave the products shown in Table I. These nitrosyl complexes, which are nonconducting in nitromethane, are soluble in benzene, chloroform, or dichloromethane and are only slightly soluble in methanol or hexane. The complexes are structurally analogous to the aryldiazo complexes, $Ir(PPh_3)_2(CO)ClX(N_2Ar)$, reported by Haymore and Ibers.[11] Compared to the ν(NO) for **1** at 1700 cm^{-1}, the ν(NO) for the complexes $Ir(PPh_3)_2(CO)ClX(NO)$ (**3**) are in the 1520-1560-cm^{-1} region.

Like other complexes formed by the addition of nucleophiles to five-coordinate Ir(III) complexes,[12] it is likely that **3** initially has an octahedral structure with the added ligand X trans to the trans directing NO^- ligand and with PPh_3 ligands trans to each other. In an ionizing solvent, however, extensive rearrangement may be expected.[12e] The complexes have ν(CO) at 2050 ± 10 cm^{-1}.

When stirred in benzene under oxygen the compounds $(Ir(PPh_3)_2(CO)ClX(NO)$ are converted to the nitrato complexes $Ir(PPh_3)_2(CO)ClX(NO_3)$ (**4**), which can be isolated as crystals upon the addition of hexane. These nitrato compounds have ir frequencies[13] at 1520 m, 1250 vs, and 950 cm^{-1} (KBr). There was no ir spectral indication of the formation of nitro or nitrito complexes (vide infra). The nitrosyl complexes, **3**, are gradually air-oxidized even in the solid state to the corresponding nitrates, **4**.

The kinetics of oxygenation of **3** was studied by measuring the change in absorbance in the 380-410-nm region using pseudo-first-order conditions with oxygen at a partial pressure of 619 Torr (8.11×10^{-3} M)[14] and the iridium complexes at $5 \pm 2 \times 10^{-4}$ M. The kinetic data presented in Table I indicate that the rates of oxygenation decrease with X as I > Br > Cl > NCS > NCO > N_3, which is roughly the order attributable to decreasing electron release by X. If only electronic contributions are important the rate for the N_3 complexes is anomalously low, perhaps as a result of steric contributions from the bulky PPh_3 and the bent $Ir-N_3$ system. It is likely that oxygenation proceeds by electrophilic attack of dioxygen on the NO^- ligand such as has been proposed for reactions of cobalt nitrosyls,[5] followed by rearrangement of the N-coordinated O-N-O-O moiety.

When a dichloromethane solution of **1** was stirred under oxygen for 12 hr, no noticeable reaction was observed. In the presence of pyridine or picoline, reaction of **1** with oxygen was rapid, giving a mixture[15] of nitrato, nitro, and nitrito complexes.

The enhanced oxidation of the NO^- ligand in **1** in the presence of base or X^- has been observed, but reasons for the exclusive nitrato formation in the presence of X^- as contrasted to formation of nitrato, nitrito, and nitro complexes in the presence of pyridine remain to be elucidated. We are continuing studies on the accelerating influence of a sixth ligand on the reactions of five-coordinate nitrosyl complexes with other electrophiles.

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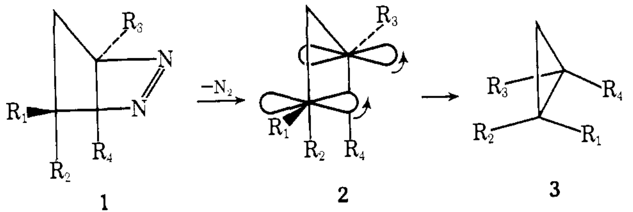
The Synthesis, Absolute Configuration, and Stereochemistry of Thermal Decomposition of (+)-(3*R*,5*R*)- and (+)-(3*R*,5*S*)-3-Ethyl-5-methyl-1-pyrazolines

Sir:

Thermal decomposition of *cis*- and *trans*-3,5-dimethyl-1-pyrazolines (**1C** and **1T**) proceeds with predominant single inversion of stereochemistry.[1] This observation provided the first experimental evidence for the existence of simply substituted π-cyclopropanes or "0,0" diradicals (e.g., **2**), and for their predicted preference for conrotatory closure.[2] However, the requirement that planar intermediate **2** give achiral products has never been adequately tested, because a complete elucidation of the stereochemistry of this reaction via the use of compounds **1C** and **1T** is precluded by the fact that **1C** and **3C** are meso diastereomers and are therefore incapable of exhibiting optical activity even if formed via chiral intermediates. Stimulated by the observation that optically active **1T** does in fact give rise to **3T** having significant optical activity,[3] we have now carried out a study of the thermal decomposition of optically active *cis*- and *trans*-3-ethyl-5-methyl-1-pyrazolines (**4C** and **4T**). This system is not subject to the loss of stereochemical information caused by the existence of meso diastereomers, and it provides results which indicate that the present understanding of the mechanism of 1-pyrazoline thermal decomposition (and perhaps of thermal decomposition in general) will require substantial revision.



1C and **3T**, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
1T and **3C**, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$

Optically active **4C** and **4T** were prepared by methods analogous to those used by Crawford and coworkers[4] and their optical purities and absolute configurations established and then confirmed by the double correlation outlined in Chart I. Absolute configurations and maximum rotations of the cyclopropane products **5C** and **5T** have been previously established.[5] Product distributions from the gas-phase thermal decomposition of **4C** and **4T** (Table I) correlate very closely with those observed[1a] from **1C** and **1T**, suggesting that changing one substituent from CH_3 to CH_2CH_3 has a negligible effect on the decomposition mechanism.

The complete stereochemical results of the decomposition of optically active **4C** and **4T**, corrected to 100% optical pu-