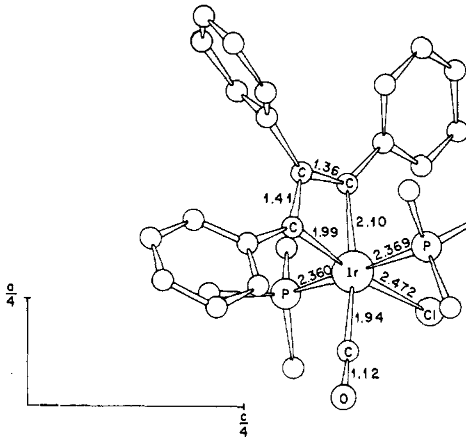

Figure 1. The $[(C_3(C_6H_5)_3)IrCl(CO)(P(CH_3)_3)_2]^+$ ion as viewed along the crystallographic *b* axis. Standard deviations are as follows: Ir–P, Ir–Cl, 0.005 Å; Ir–C, 0.015 Å; C–C, 0.02 Å.

with unit cell dimensions $a = 9.808$ (1), $b = 17.758$ (2), $c = 19.971$ (3) Å; $Z = 4$; $D_{calcd} = 1.61$ g cm^{-3}; $D_{obsd} = 1.62$ g cm^{-3}. The moving-crystal, moving-counter technique and Cu Kα radiation were used to collect intensity data ($2\theta_{CuK\alpha} \leq 140°$). The structure was solved using standard heavy-atom techniques and refined to a conventional R factor of 0.060 for the 3257 reflections whose intensities were greater than two times their estimated standard deviations.

Solution of this structure affords a singularly significant fact: the cyclopropenium ring is opened by and adds oxidatively to $IrCl(CO)(P(CH_3)_3)_2$ to form the product, I. In this molecule the iridium(III) ion has a distorted octahedral environment formed by two trans phosphine groups, a chlorine atom, carbon monoxide, and two carbon atoms of the propenium fragment (Figure 1). An interior C–Ir–C angle of 64.5 (3)° represents the greatest angular distortion from idealized octahedral geometry in the complex. Both of the Ir–Cl and Ir–C(O) distances are long since they are trans to a σ-bonded carbon atom. A trans lengthening of similar magnitude was found for Ir(III)–Cl bonds in $[Ir(CO)_2Cl_2(CH_3)]_2$[3] and the benzylacetophenone complex, $IrCl_2(C_{15}H_{13}O)((CH_3)_2SO)_2$,[4] where the chlorine atom is trans to a methyl and methylene group, respectively. The two iridium–carbon bonds within the iridocycle differ in length by 0.11 Å which is presumably due to the dissimilar trans influence of the CO and Cl groups. Mason and coworkers have noted an analogous asymmetry in metal–carbon bond lengths arising from different trans ligands in the π-allyl derivatives $(\pi\text{-}CH_3C_3H_4)Pd(Cl)(P(C_6H_5)_3)$[5] and $[(\pi\text{-}C_3H_5)_2RhCl]_2$.[6]

The metallocyclic portion of the molecule is essentially planar (disregarding the substituent phenyl groups) and the two iridium–carbon bond lengths are within the range expected for an Ir(III)–C(sp^2) distance when there is no appreciable dπ–pπ interaction. An average value of 1.385 (15) Å was found for the two carbon–carbon distances in the propenium fragment, which is very nearly equal to that determined (1.373 (5) Å) for the uncomplexed cyclic ligand in $(Ph_3C_3)(ClO_4)$.[7] The transannular distances of 2.61 (Ir–C) and 2.12 Å (C–C) are dictated mainly by the stereochemistry of a planar four-membered ring system and indicate little or no bonding interaction. Inasmuch as there is no evidence for a significant π interaction between the carbon and iridium atoms, the two π electrons associated with the original $(C_3Ph_3)^+$ species appear to remain localized on the propenium group.

To our knowledge this is the first authenticated example of the oxidative addition of a metal ion across a carbon–carbon bond. We draw attention to the striking similarity between this complex and the intermediate recently postulated[8] for the valence isomerism of cubane and its derivatives. Other metal-atom-induced cleavages of three-membered ring systems are known, such as the formation of the cyclopropane derivative,[9] $[PtCl_2(C_3H_6)]_4$, and the reaction[10] of $C_3H(C_6H_5)_3$ with $PdCl_2(C_6H_5CN)_2$ to give a π-allylic derivative of palladium(II). Coordinatively unsaturated d^{10} complexes might also be expected to react with $(C_3Ph_3)^+$, and studies along these lines are in progress.

Acknowledgment. We are grateful to the National Science Foundation for its support of this work.

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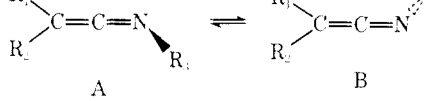
Ketenimines. Geometry and Barriers to Racemization

Sir:

In continuation of our studies on barriers to configurational interconversion in cumulenes,[1,2] we wish to report on the geometries and barriers to racemization of the ketenimines Ia and Ib.



Ia, R_1 = phenyl; R_2 = isopropyl; R_3 = phenyl
Ib, R_1 = methyl; R_2 = isopropyl; R_3 = phenyl

In analogy with carbodiimides,[2] ketenimines can be expected to have a linear C=C=N moiety and dihedral angles of 90° between the C and N substituents (*e.g.*, R_1 and R_2 in I). A ketenimine with different substituents R_1 and R_2 should be chiral, and in such a compound an isopropyl substituent should have diastereotopic methyl groups which might be differentiated by nmr.

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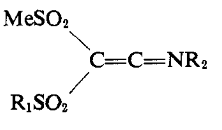
Simon, Kerek, and Ostrogovich,[3] using the Hückel molecular orbital method, estimated that the barrier to thermal racemization of ketenimines as well as of carbodiimides should not be higher than 10 kcal/mol.

Structure determinations of alkyl- or aryl-substituted ketenimines are lacking. An X-ray analysis of the crystal structure of ketenimines IIa and IIb, which have strongly electron-withdrawing sulfonyl substituents on carbon, showed a virtually linear C=C=N—C chain with an unusually short C=N bond (1.15 Å) having essentially triple bond character.[4,5] For IIc an angle of 145° between the bonds of the nitrogen atom was reported, the C=N bond (1.17 Å) being still too short for a double bond.[6]



IIa, R_1 = methyl; R_2 = methyl
IIb, R_1 = phenyl; R_2 = methyl
IIc, R_1 = methyl; R_2 = ethyl

At −99° and above the 100-MHz proton resonance spectrum[7] of a 3% solution of Ia[8–11] in 1 : 1 vinyl chloride–chlorodifluoromethane shows a doublet for the methyl protons with 6.6-Hz coupling to the methine protons. At −102° the lines are broadened greatly, and on further lowering of the temperature they separate into a pair of doublets with a chemical-shift difference of 4 Hz at −113° (Figure 1).

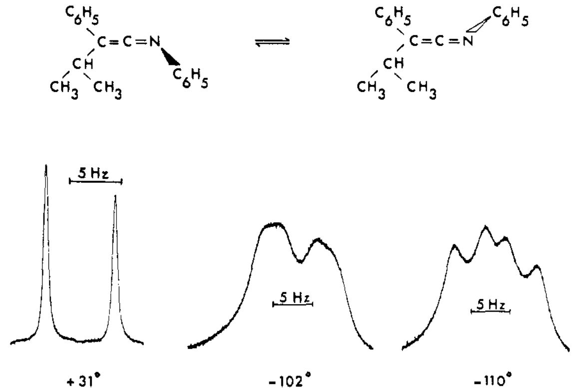


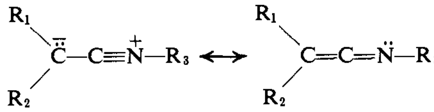
Figure 1. 100-MHz spectra of the methyl protons of phenylisopropylketene phenylimine (Ia) at various temperatures.

Under the same experimental conditions the ketenimine Ib[8] shows two methyl doublets with markedly temperature-dependent chemical-shift differences (3.9 Hz at −117°, 2.6 Hz at −71°), merging to one doublet (J = 6.7 Hz) at −51°.

These results confirm[12] the expected dissymmetric geometry for the ketenimines Ia and Ib and demonstrate the rapid interconversion of the enantiomers A and B at room temperature. The free energies of activation for racemization as calculated at the coalescence temperatures are 9.1 ± 0.2 kcal/mol for Ia and 12.2 ± 0.3 kcal/mol for Ib.[13]

Thus, the barriers to recemization in ketenimines are considerably higher than the barrier found for diisopropylcarbodiimide (6.7 ± 0.2 kcal/mol).[2] There seems to be a marked influence of the substituents: replacement of the phenyl group in Ia by CH_3 to give Ib raises the barrier by about 3 kcal/mol.

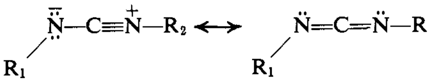
As for the racemization mechanism, a linear polar transition state symbolized by (IIIa ↔ IIIb) seems to be most likely.



IIIa IIIb

This transition state would account for the observed substituent effect. In extreme cases with strongly electronegative groups on carbon, such as IIa and IIb, the linear form (IIIa ↔ IIIb) becomes energetically favored over the bent geometry I.[4,5]

If an analogous transition state (IVa ↔ IVb) is assumed for the interconversion of carbodiimides,[14] the differences in the barriers to racemization of ketenimines and carbodiimides should reflect the difference in electronegativities of nitrogen and carbon in imines and olefins, respectively. One would also predict that the barrier to racemization of an aryl-substituted carbodiimide might be considerably lower than that found for diisopropylcarbodiimide (6.7 kcal/mol).[2]



IVa IVb

Acknowledgment. This work was supported by the United States Public Health Service.

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[8] Ketenimines Ia and Ib were synthesized in 60 and 62% yields from 2-phenyl-3-methylbutanoic acid[10] and 2,3-dimethylbutanoic acid,[11] respectively, *via* the iminochlorides according to the general method described by Stevens and French.[9] Ketenimine Ia is a yellow oil, bp 112–113° (0.18 mm). Ib is a greenish yellow oil, bp 57–58° (0.16 mm).

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[16] Carbodiimides. VI. Carbodiimides. V: see ref 2.

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Hexa(dimethylgermanium)tetraphosphide. A New Germanium–Phosphorus Cage Molecule

Sir:

We wish to report the preparation and characterization of hexa(dimethylgermanium)tetraphosphide,