of the backbone of gramicidin S have correlation times equal to the molecular reorientation time. Despite this, extensive reevaluation of all the assumptions behind this method are required; until then the best accuracy that can be claimed for the interproton distances is 2.0 ± 0.2 Å, even though the precision (~0.04) of the measurements is much higher.

Model building (3 cm/Å) assuming $\psi = -120°$ for a classical type II′ β turn yields 2.23 and 2.57 Å for these distances while Dygert et al.[12] using semiempirical calculations determined these distances as 2.24 and 2.21 Å and the ψ angle as −137°. The interproton distances of 2.0 ± 0.2 Å determined from the NOE measurements plus the independent determination of the ratio of these distances (eq 3) agree best with the latter and indicate a ψ (Phe) of $-130° \pm -15°$. Thus the protons of the Pro $C^{\delta}H$--Pro $C^{\delta}H$--Phe $C^{\alpha}H$ moiety approach within their Van der Waals contact distance and appear to be a tightly packed system. This suggests that any χ_4 motions of the Pro ring system will be coordinated with χ rotation of the Phe residue.

This report confirms quantitatively what was previously suggested and qualitatively shown:[1] NOE's can be used to determine dihedral angles in peptides, can specifically give the previously unmeasured angle ψ to reasonable accuracy, and can be used quantitatively as criteria for common conformational features of peptides such as β turns, extended structures, and helices. This approach offers considerable promise for the future of peptide (and protein) conformational analysis since now a combination of NMR techniques exists which can produce a number of measured parameters equal to or slightly greater than the number of unknown dihedral angles to be determined.

Acknowledgments. This work was supported by grants from the NIH (AM 18604), NSF (BMS 74.23819 and PCM 7713976), and the College of Agriculture and Life Sciences as well as the Enzyme Institute (Postdoctoral Training grant AM 07049 for C.R.J.) of the University of Wisconsin. Partial expenses for the Bruker WH 270 campus facility were provided by the Graduate School Research Committee and the University of Wisconsin Biomedical Research Grant No. RR. 07098.

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Claude R. Jones, Cynthia T. Sikakana
Mei-chang Kuo, William A. Gibbons*
Department of Biochemistry, University of Wisconsin
Madison, Wisconsin 53706
Received April 10, 1978

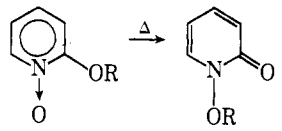
Effect of Pressure on Concerted and Stepwise Sigmatropic Shifts[1]

Sir:

Innumerable data are now available[2] supporting the conjecture[3] that concerted cycloadditions should have smaller transition states than the diradicaloid stepwise analogues, the simple reason being that the former have two new bonds in the process of formation and the latter one. While this criterion is subject to confusion by special features such as a highly dipolar starting component[4] or intermediate,[5] when these considerations have been taken into account, there is little room for doubt about the mechanism.

Similar arguments should be possible about other types of pericyclic reactions. Thus, concerted sigmatropic shifts should involve primarily the formation of a new bond and hence a volume contraction, whereas stepwise shifts characterized by initial bond cleavage to give radicals should be characterized by a volume expansion. The concerted reactions should therefore be accelerated, and the stepwise ones should be retarded. To date few of these reactions have been studied. Claisen[6,7] and Cope[7,8] rearrangements have negative activation volumes and hence they fit their description as concerted in this respect; stepwise shifts via diradicals are indicated by pressure-inhibited rates in the racemization of benzyl phenyl sulfoxide[9] and in the rearrangement of *N*-(1-cyanocyclohexyl)pentamethyleneketenimine to bi(1-cyanocyclohexyl).[10] No examples have been reported, however, of chemically very similar sigmatropic shifts of contrasting mechanism, such as was done by Stewart,[11] for example, for cycloadditions.

The thermal 1,4 shift of 2-alkoxypyridine *N*-oxide to *N*-alkoxy-2-pyridone[12] offers such a contrast: with R as benzyl (I), the rearrangement is concerted, but with benzhydryl (II)



it proceeds via diradicals. Both reactions have rates virtually independent of solvent, but only the latter exhibits strong CIDNP signals as it progresses.

The pressure effects have now been measured at 100 °C in diglyme solution. The benzyl reaction was followed by NMR analysis and the benzhydryl by means of UV; the pressure

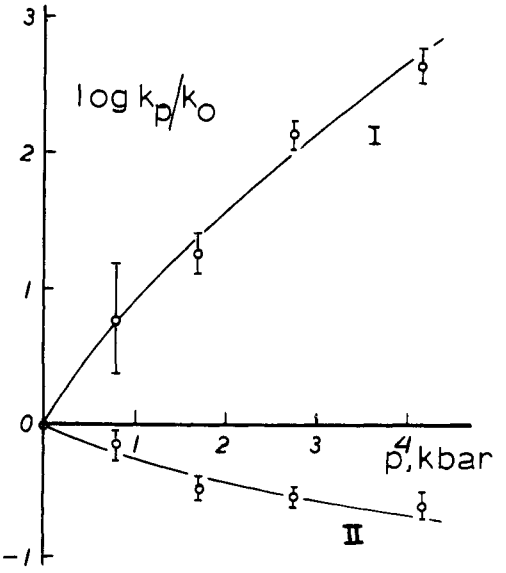


Figure 1. Effect of pressure on the rearrangement rates of substrates I and II.

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range was 4 kbar. The results, shown in Figure 1, may be summarized by the statement that the activation volume for the concerted shift (I) equals -30 ± 5 cm^3/mol and that for the stepwise reaction (II) is $+10 \pm 2$ cm^3/mol. These observations clearly confirm that this activation parameter provides a criterion for concertedness in sigmatropic shifts as well as for cycloadditions.

Acknowledgment. The National Science Foundation generously supported this investigation.

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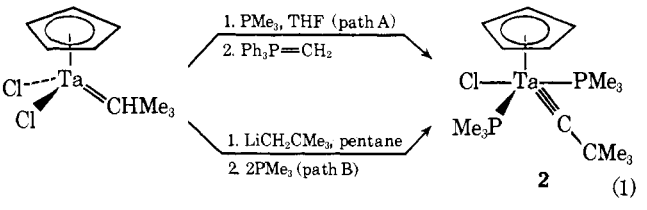
W. J. le Noble,* M. Rajaona Daka
Department of Chemistry, State University of New York Stony Brook, New York 11794
Received March 14, 1978

Multiple Metal–Carbon Bonds. 10.[1] Thermally Stable Tantalum Alkylidyne Complexes and the Crystal Structure of Ta(η^5-C_5Me_5)(CPh)(PMe_3)$_2$Cl

Sir:

Alkylidene complexes of niobium and tantalum have been prepared by deprotonating (formally[2] or actually[3]) the α-carbon atom of an alkyl ligand in a M^{5+} complex. We now can prepare thermally stable Ta neopentylidyne[4,5d] complexes similarly by deprotonating a cationic neopentylidene complex. Both neopentylidyne and benzylidyne complexes can be prepared more cleanly by accelerating abstraction of the alkylidene α-hydrogen atom by the alkyl ligand in neutral alkyl/alkylidene complexes with trimethylphosphine.

Addition of 1 mol of PMe_3 to red $TaCp(CHCMe_3)Cl_2$[7] in toluene yields the sparingly soluble yellow adduct, $TaCp(CHCMe_3)Cl_2(PMe_3)$ (**1**).[8a] In THF in the presence of 3–5 additional mol of PMe_3, **1** reacts with $Ph_3P{=}CH_2$ to give $[Ph_3PCH_3]^+Cl^-$ (~90% yield). Removing the THF and extracting the residue with pentane gives moderately soluble, pale yellow, crystalline **2** in 60% crude yield (30% yield of pure, recrystallized **2**; eq 1, path A). Calcd for $TaC_{16}H_{32}P_2Cl$: C, 38.23; H, 6.41; Cl, 7.05. Found: C, 38.09; H, 6.26; Cl, 6.99. We postulate that $[TaCp(CHCMe_3)Cl(PMe_3)_2]^+Cl^-$ is an intermediate from which a proton is removed by $Ph_3P{=}CH_2$ to give **2** (cf. the reaction of $TaCp_2(CHCMe_3)Cl$ with PMe_3 to give[1] $[TaCp_2(CHCMe_3)(PMe_3)]^+Cl^-$ and the deprotonation of $[TaCp_2Me_2]^+BF_4^-$ by $Me_3P{=}CH_2$ to give $TaCp_2(CH_2)(CH_3)$[3]). Yellow **2** is indefinitely stable at 25 °C in solution. In the solid state it reacts only slowly with oxygen but is more sensitive to water or other protic solvents. It sublimes with little decomposition at 100 °C and 1 μ and is a monomer in cyclohexane (mol wt, 527 cryoscopically; theory, 503).



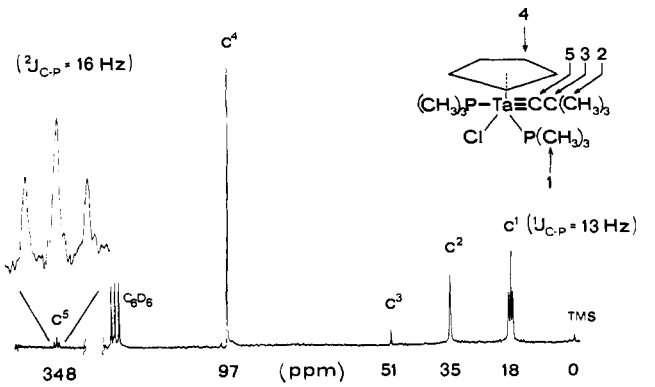
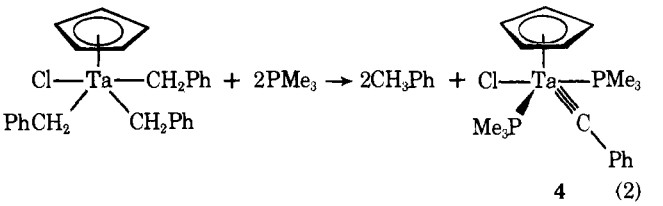


Figure 1. The 22.63-MHz $^{13}C\{^1H\}$ NMR spectrum of Ta(η^5-C_5H_5)($CCMe_3$)(PM_3)$_2$Cl (**2**).

The $^{13}C\{^1H\}$ NMR spectrum of **2** is shown in Figure 1. The most important feature is the 1:2:1 triplet at 348 ppm due to the neopentylidyne α-carbon atom coupled to two equivalent phosphorus nuclei. Some coupling of the neopentyl methyl carbon atoms (C^2) to phosphorus can also be seen. In the gated decoupled spectrum the resonances for C^5 and C^3 are broad (owing to long-range CH coupling), but every other peak is split into the appropriate multiplet. The neopentylidyne C^α resonance is ~100 ppm farther downfield than the neopentylidene C^α resonance in $TaCp(CHCMe_3)Cl_2$[7] and related molecules[1,2] and is in the same region where the alkylidyne α-carbon resonances in group 6 complexes such as Br-$(CO)_4W{\equiv}CPh$ are found.[5] The ^1H NMR spectrum[8b] also suggests that the phosphine ligands are equivalent.

The reaction of $LiCH_2CMe_3$ with $TaCp(CHCMe_3)Cl_2$ at 25 °C in pentane gives $TaCp(CHCMe_3)(CH_2CMe_3)Cl$ (**3**) in 85–90% isolated yield as a pentane-soluble, thermally stable, sublimable, orange oil.[9] On adding PMe_3 to a pentane solution of **3** at 25 °C 1 mol of neopentane evolves immediately and **2** forms quantitatively (eq 1, path B); no other products can be seen by ^1H NMR. We believe that PMe_3 coordinates to **3** to give a pseudo-five-coordinate complex in which abstraction of the neopentylidene ligand's α-hydrogen atom by the neopentyl ligand is more favorable than it is in pseudotetrahedral **3**. It is also possible that abstraction of an α-hydrogen atom from the *neopentyl* by the *neopentylidene* ligand is similarly "accelerated", but, since this reaction is degenerate, we cannot tell which α-abstraction process is faster.

The reaction of thermally unstable $TaCp(CH_2Ph)_3Cl$[10] in benzene with 2 mol of PMe_3 gives less soluble, red $TaCp(CH_2Ph)_3Cl(PMe_3)$ (by ^1H NMR) which dissolves completely on heating to 60 °C for 2 h to give an orange solution which contains 2 mol of toluene (by ^1H NMR and GLC) and **4** (eq 2). We do not yet know whether pseudo-six-coordi-



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