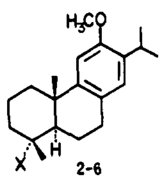
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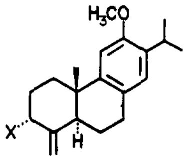
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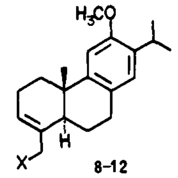
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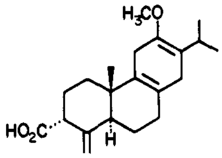
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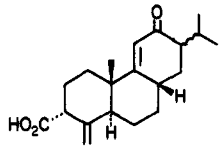

17

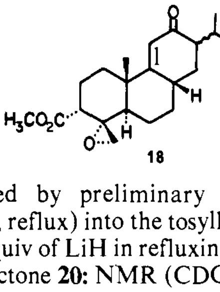
2 X = CO_2CH_3
3 X = CO_2H
4 X = NCO
5 X = $N(CH_3)_2$
6 X = $N(CH_3)_2O$

7 X = H
13 X = $CH_2SC_6H_5$
14 X = CHO
15 X = COOH

8 X = OH
9 X = Cl
10 X = SC_6H_5
11 X = $(CH_3SC_6H_5)^+$, BF_4^-
12 X = $CH_2{=}SC_6H_5$

homologated thioether **13**. Transformation into aldehyde **14** (34% from **10**) was achieved by α-monochlorination of the thioether unit (NCS, CCl_4, room temperature), formation of the monothioacetal by treatment with MeOH (ether, 0 °C), and final treatment with $I_2/NaHCO_3$ (dioxane-H_2O, room temperature). Oxidation of **14** ($NaClO_2/NH_2SO_3H$, THF-H_2O, 0 °C) afforded the unsaturated acid **15** (mp 80-84 °C): NMR (CCl_4) δ 0.98 (s, 3 H, 20-CH_3), 1.16 (d, J = 7.0 Hz, 6 H, 16-CH_3 and 17-CH_3), 3.70 (s, 3 H, 12-OCH_3), 4.77, 4.95 (s, 1 H, 19-CH_2), 6.52 (s, 1 H, 11-CH), 6.67 (s, 1 H, 14-CH).

On subjection to the action of 86 equiv of Li bronze in *t*-BuOH-Et_2O-NH_3 for 4 h, **15** was reduced to the dihydroanisole **16** [NMR (CCl_4) inter alia δ 3.45 (s, 3 H, 12-OCH_3), 4.75, 4.97 (s, 1 H, 19-CH_2)], which was hydrolyzed by 2-h reflux in 6 N $HClO_4$/THF, giving the conjugated ketone **17** [NMR (CCl_4) inter alia δ 4.74, 4.94 (s, 1 H, 19-CH_2), 5.77 (m, 1 H, 11-CH)]. Oxidation of the latter with 3,5-dinitroperbenzoic acid (CH_2Cl_2, room temperature, 13 h), followed by exposure to CH_2N_2/Et_2O at 0 °C, provided (38% from **14**) epoxy ester **18**: NMR (CCl_4) inter alia δ 3.68 (s, 3 H, 18-CO_2CH_3), 5.72 (m, 1 H, 11-CH). Through the action of LiN-*i*-Pr_2/THF (−78 °C), ester **18** presumably suffers elimination to the γ-hydroxy-α,β-unsaturated ester, which spontaneously cyclizes (46%) to the butenolide **19**: NMR (CCl_4) inter alia δ 4.60 (m, 2 H, 19-CH_2), 5.78 (m, 1 H, 11-CH). C-ring reduction of **19** to the conjugated diene level was managed by preliminary conversion ($TsNHNH_2$/HCl, MeOH, reflux) into the tosylhydrazone followed by the action of 25 equiv of LiH in refluxing $C_6H_5CH_3$,[10] generating (39%) trienelactone **20**: NMR ($CDCl_3$) δ 0.88 (s, 3 H, 20-CH_3), 1.04 (d, J = 6.8 Hz, 6 H, 16-CH_3 and 17-CH_3), 4.69 (m, 2 H, 19-CH_2), 5.69 (m, 2 H, 11-CH and 12-CH). In keeping with the biosynthetic suggestions of Manchand and Blount,[2] the diene moiety of **20** was subjected to attack by $^1O_2$ (generated by irradiation of $^3O_2$ in the presence of methylene blue), giving a stereomeric mixture of peroxides **21** (~2:1 9,13-α:β). After separation of **21** on a silica gel column, the β-peroxide was heated in refluxing xylene for 12 h. The product, formed in nearly quantitative yield and crystallized from ether-ethyl acetate, was found to be identical with natural stemolide, on the basis of IR, NMR, CD ($[\theta]_{223\ \mathrm{nm}}$ +15 300, $[\theta]_{246\ \mathrm{nm}}$ −4800), mass spectral, as well as melting point (230-232 °C) and mixture melting point (230-232 °C) comparisons.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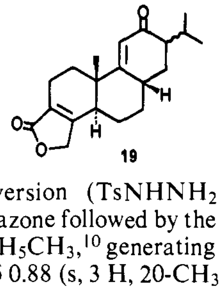
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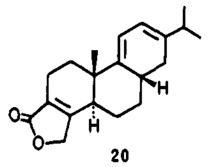
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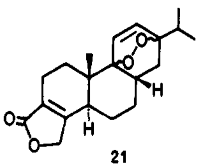
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E. E. van Tamelen,* E. G. Taylor
Department of Chemistry, Stanford University
Stanford, California 94305

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Spectroscopic Characterization of an Electrophilic Transition-Metal-Methylene Complex, η^5-$C_5H_5[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe{=}CH_2^+$

Sir:

The preparation of transition-metal-carbene complexes which lack direct heteroatom stabilization of the electrophilic carbene carbon center is of interest owing to the high reactivity of these species in comparison with that of heteroatom-stabilized systems.[1] To date, Schrock[2] has reported the only successful isolation of an unsubstituted methylene complex, $Cp_2TaCH_3(CH_2)$; however, based on its reactivity, the carbene carbon in this complex is clearly *nucleophilic* in nature. In the electrophilic series, methylene complexes have been frequently postulated as intermediates, but their direct observation has most often been elusive. For example, Pettit and Jolly,[3] Green,[4] and Brookhart[5] have suggested **1a** as a transient species formed on acid treatment of $Cp(CO)_2Fe$-CH_2OCH_3, while Davison[6] and Flood[7] have proposed **1b** as an intermediate formed from $Cp(CO)PPh_3Fe$-CH_2OR in acid-catalyzed methylene transfer to olefins and SO_2 insertion into the C—O bond, respectively. Pettit[8] has recently suggested the formation of the

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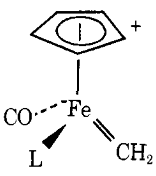
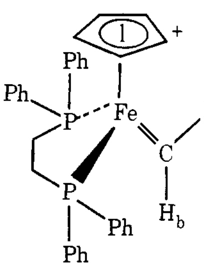


1a, L = CO
b, L = PPh_3



2

$Cp(Ph_2PCH_2CH_2PPh_2)Fe{=}CH_2^+$ ion (**2**) from acid treatment of the ether precursors as judged by production of ethylene and by methylene transfer to cyclohexene. Most recently, Gladysz has reported spectral observation of the cationic complex $CpRe(PPh_3)(NO)CH_2^+$.[9]

We report here the generation and spectroscopic characterization of **2**, which represents to date the only first-row transition-metal-methylene complex to be so observed. Treatment of $Cp(Ph_2PCH_2CH_2PPh_2)Fe\text{-}CH_2OCH_2CH_3$ in CD_2Cl_2 or $CD_2Cl_2\text{-}SO_2$ at −78 °C with 2-20 equiv of either trifluoroacetic acid or triflic acid results in formation of a homogeneous dark red solution of the cationic methylene complex **2**. The ^1H NMR spectrum ($CHDCl_2$, internal standard δ 5.30) of **2** at −90 °C exhibits a doublet at δ 3.51 (4 H) for the methylene protons of the diphos ligand, a singlet at δ 5.63 (5 H) for the cyclopentadienyl resonance, a multiplet at δ 7.3-7.7 (20 H) for the aryl protons and, most convincing of the carbene structure, two one-proton resonances at δ 13.89 (t, H_b, $J_{^{31}P-^1H}$ = 14 Hz) and 17.29 (H_a, br s) for the two nonequivalent methylene protons.[10] The H_a and H_b assignments suggested are based on comparison with the benzylidene hydrogen in $Cp(CO)LFe{=}CHC_6H_5^+$ [**3**, L = CO (**a**), PPh_3 (**b**)][5] which is postulated to be syn to the cyclopentadienyl ring, appears at ca. δ 17, and is only weakly coupled (∼1 Hz) to phosphorous in **3b**. The ^{13}C NMR parameters confirm completely the carbene structure. The most definitive feature is the characteristic low-field resonance of the carbene carbon[1,11] at 317.5 ppm ($J_{^{31}P-^{13}C}$ = 32 Hz, $J_{^{13}C-^1H}$ = 140 Hz; other resonances appear at 137.5-128.7 (phenyl carbons), 91.7 (C_5H_5), and 29.5 ppm ($\text{-}CH_2CH_2\text{-}$). The shift of the carbene carbon is in accord with that observed for benzylidene complexes **3a** and **3b** (342 and 341 ppm) taking into account the substituent effect of the phenyl group.[5]

The nonequivalence of the methylene hydrogens confirms that the H-C-H plane of the carbene ligand lies perpendicular to the plane of the cyclopentadienyl ligand as proposed for the analogous benzylidene complexes **3a** and **3b**,[5] as determined by X-ray crystallography for a structurally similar manganese complexes[12] and as calculated by Hoffmann[13] for the dicarbonyl methylene complex, **1**. The barrier to rotation about the iron-carbene carbon bond can be estimated from variable-temperature ^1H NMR experiments. As illustrated in Figure 1, at temperatures above ca. −80 °C, the signals at δ 13.9 and 17.3 begin to broaden, coalesce at −40 °C and sharpen to a two-proton triplet ($J_{^1H-^{31}P}$ = 7 Hz) at 25 °C. (This behavior is reversible; however, the methylene complex is stable for only 1-2 at 25 °C.) The first-order rate constant for site exchange can be estimated as 35 s^{-1} at −65 °C using the slow exchange approximation, 766 s^{-1} at −40 °C using the coalescence formula, and ∼1 × 10^5 at −14 °C using the fast exchange approximation.[14] All rates correspond to a free energy of activation, $\Delta G^{\ddagger}$, for bond rotation of 10.4 ± 0.1 kcal/mol. The coalescence temperature is not affected by a change in acidity (trifluoroacetic versus triflic) or a tenfold change in acid concentration. This observation suggests the two-site averaging process must be due to simple bond rotation and not caused by collapse to a covalent intermediate which rotates and reionizes to effect exchange.

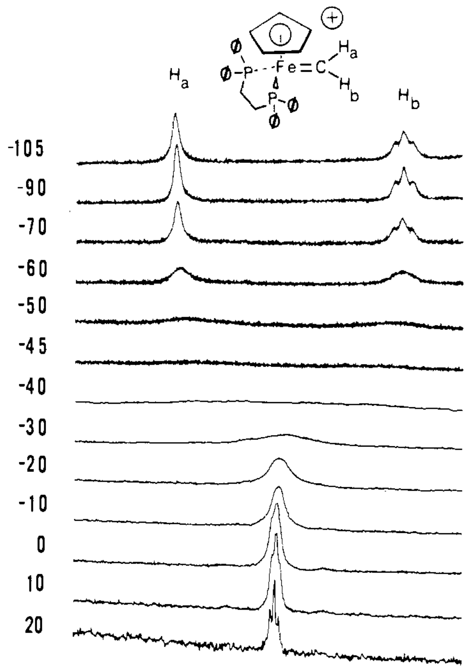


Figure 1. Variable-temperature ^1H NMR of the methylene protons of $\eta^5\text{-}C_5H_5[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe{=}CH_2^+$ in $CD_2Cl_2\text{-}CF_3COOD\text{-}SO_2$ solution.

The observed barrier for **2** compares favorably with the barrier calculated by Hoffmann[12] for the dicarbonyl methylene complex of 6.2 kcal/mol. Increased back-bonding to the methylene ligand would result upon replacement of the CO ligands by the phosphine ligands and thus the barrier to rotation is expected to be greater in **2** relative to **1a**.

The stability of the methylene complex **2** is in marked contrast to the dicarbonyl analogue, **1**, which disproportionates even at −90 °C.[5] This increased stability may be the result of decreased electrophilicity of the carbene carbon due to increased back-bonding to the methylene ligand and/or the result of steric retardation of a bimolecular disproportionation reaction. Although we have been unable thus far to isolate crystalline salts of **2**, some preliminary studies regarding the reactions of **2** have been carried out in methylene chloride-trifluoroacetic acid solution. Complex **2** converts olefins into cyclopropanes as shown by the isolation of methylene adducts of ethyl vinyl ether (98% yield), 1-hexene (30%), and cyclohexene (∼10%). Additional studies of reactivity are in progress. The high reactivity of ethyl vinyl ether relative to 1-hexene clearly illustrates the electrophilic character of the methylene complex while decreased reactivity of cyclohexene relative to 1-hexene suggests a moderate steric influence on the rate of methylene transfer.

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M. Brookhart,* James R. Tucker
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Thomas C. Flood,* John Jensen
Department of Chemistry
University of Southern California
Los Angeles, California 90007

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Pressure Effects on the Thermal Cis → Trans Isomerization of 4-Dimethylamino-4′-nitroazobenzene. Evidence for a Change of Mechanism with Solvent

Sir:

The mechanism of the thermal isomerization of *cis*-azobenzenes has attracted considerable interest. The reaction may proceed via rotation about the N=N bond or via inversion of one of the nitrogen atoms. Although a theoretical calculation[1] on unsubstituted azobenzene has supported the inversion mechanism, the experimental results obtained so far have been inconclusive. Thus, the enthalpy of solvent transfer[2] and the activation parameters in cholesteric liquid crystal solvent[3] were taken as evidence for the inversion and the rotation mechanisms, respectively. For push-pull-substituted azobenzenes, large kinetic solvent effects were observed.[4] These results are most likely a reflection of the dipolar rotational transition state expected for these azobenzenes, The two transition states are illustrated in Scheme I for 4-dialkylamino-4′-nitroazobenzene.

Scheme I

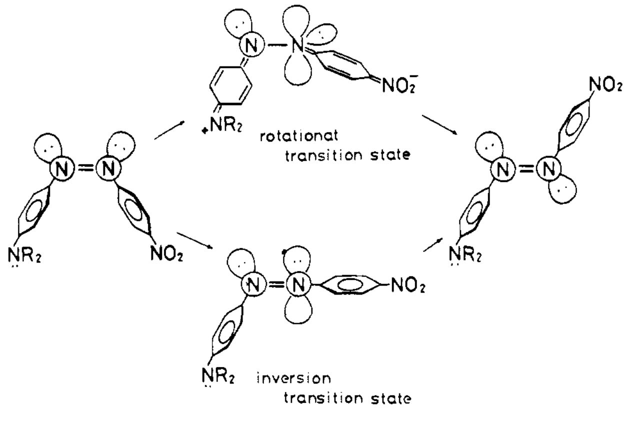

Table I. First-Order Rate Constants for the Thermal Cis → Trans Isomerization of 4-Dimethylamino-4′-nitroazobenzene at Various Pressures

benzene[a] (30 °C) pressure, bar	benzene[a] (30 °C) 10^2k, s^{-1}	*n*-hexane[a] (40 °C) pressure, bar	*n*-hexane[a] (40 °C) 10^2k, s^{-1}
1	1.78	1	1.06
200	2.12	300	1.11
400	2.43	600	1.13
600	2.81	900	1.03
800	3.15	1200	1.06
		1500	1.09
		1800	1.12
		2100	1.19

[a] Solvent.

It is now recognized[5] that the activation volume, obtained from the kinetic effect of pressure according to

$$\Delta V^{\ddagger} = -RT\left(\frac{\partial \ln k}{\partial P}\right)_T \qquad (1)$$

is quite sensitive to the polarity change of the reactant(s) during activation. For example, one may expect a fairly strong acceleration by pressure ($\Delta V^{\ddagger} \simeq -10 \sim 20\ \mathrm{cm^3/mol}$) for the rotational isomerization in the present case. On the other hand, if the inversion mechanism is operative, the pressure increase will cause little change in the rate constant. Accordingly, a high-pressure study has been undertaken for the title compound. The sample solution was contained in an inner glass cell similar to the one described by le Noble and Schlott.[6] The cell was put in a high-pressure vessel with four optical windows set in the cell compartment of a recording spectrophotometer.[7] The solution was irradiated by a filtered light beam from a 150-W tungsten projection lamp after it was brought to a desired temperature and pressure. The thermal decay of the cis isomer was followed after cutting off the irradiation by means of a manually operated shutter.

The results are shown in Table I and Figure 1. The activation volumes at 1 bar are $-22.1\ \mathrm{cm^3/mol}$ in benzene and $-0.7\ \mathrm{cm^3/mol}$ in hexane, respectively. The striking difference in pressure effects in the two solvents is totally unexpected. If the reaction proceeds via the rotational transition state, as expected from the solvent effects at 1 bar, the most negative activation volume would be expected for hexane, because the electrostrictive volume contraction is known to increase with decreasing solvent polarity.[8] Therefore, the results presented here suggest quite strongly that the reaction mechanism changes, from inversion in hexane to rotation in benzene. Table II presents the rate constants for unsubstituted azobenzene obtained

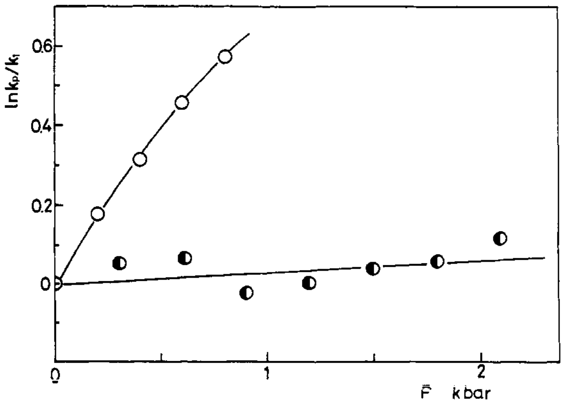

Figure 1. Pressure effects on the first-order rate constant for cis → trans thermal isomerization of 4-dimethylamino-4′-nitroazobenzene: ○, in benzene at 30 °C, ◐, in *n*-hexane at 40 °C.

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