

Figure 1. $\ln(2/1)$ vs. T^{-1} (K^{-1}) for reaction 1; cf. Table I. Points a-c represent solution experiments; points d and e refer to matrix photolyses.

Table I. Product Ratios from Ph_2C and Isobutene as a Function of Temperature^a

Temp, °C	2/1	Av dev _n ^b
0	0.243	0.008 ₄
-77	0.682	0.007 ₂
-130	3.07	0.04 ₃
-155 ^c	6.25	0.14 ₃
-196 ^c	44.6	7.57 ₆

^a Values were determined by GC⁶ and are corrected for relative detector response. ^b Average deviation of n experiments. ^c Solid isobutene matrices were formed.

kcal/mol. However, $\Delta E_{\text{app}}^{\text{a}}$ contains contributions from at least four sources: activation energies for singlet addition ($E_{\text{ad}}^{\text{a,S}}$), triplet abstraction ($E_{\text{abst}}^{\text{a,T}}$), and triplet addition ($E_{\text{ad}}^{\text{a,T}}$), as well as the differential singlet-triplet energy ($\Delta E_{\text{S-T}}$). If $E_{\text{ad}}^{\text{a,T}}$ is the largest of the activation energies,¹³ and triplet addition is neglected, then $\Delta E_{\text{app}}^{\text{a}} \sim (E_{\text{ad}}^{\text{a,S}} - E_{\text{abst}}^{\text{a,T}}) + \Delta E_{\text{S-T}}$. Taking an upper limit of 3 kcal/mol for $\Delta E_{\text{S-T}}$,¹⁴ and recalling that $\Delta E_{\text{app}}^{\text{a}} = 1.1$ kcal/mol, we estimate that $(E_{\text{abst}}^{\text{a,T}} - E_{\text{ad}}^{\text{a,S}}) \leq 1.9$ kcal/mol.¹⁴ That is, the activation energy for triplet abstraction¹⁵ is greater than that for singlet addition, but the difference is *smaller* than $\Delta E_{\text{S-T}}$.¹⁶ Thus, as temperature decreases for reaction 1, triplet abstraction gains relative to singlet addition, because the increase in triplet population more than offsets the higher activation energy needed for abstraction.

Analogous behavior may well be common for other arylcarbenes, viz., phenylcarbene,³ phenylmethylcarbene,⁴ and fluorenylidene.¹⁷ More generally, we should expect similar temperature dependent phenomena with other carbenes and for other types of competitive singlet and triplet reactions.^{18,19}

Finally, it will be noted from Figure 1, that *less* olefin is formed in the -196 °C matrix experiment (point e) than is predicted by simple extrapolation of the solution points: 2/1 predicted by extrapolation of points a-c is ~290 at -196 °C, whereas the observed value is 44.6. With Ph_2C and isobutene, it is clear that temperature effects (i.e., differential energy factors) are largely, if not exclusively, responsible for the ultimate dominance of the triplet abstraction reaction in both very cold solutions and frozen matrices. The suspicion is strong that temperature effects must also be major influences in the previously observed, analogous reactions of phenylcarbene³ and phenylmethylcarbene.⁴

Acknowledgments. We thank the National Science Foundation and the Public Health Service (Grant CA-14912 from the National Cancer Institute) for financial support, J.K.H.

acknowledges the receipt of a National Science Foundation Undergraduate Research Participation stipend. We are also grateful to Dr. Dorothy Z. Denney for ¹³C NMR spectra and to Professors Rolfe Herber and G. L. Closs for helpful discussions.

References and Notes

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- (2) (a) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, Jr., R. H. Levin, and M. B. Sohn in "Carbenes", Vol. I, M. Jones, Jr., and R. A. Moss, Ed., Wiley, New York, N.Y., 1973, pp 73-79; (b) G. L. Closs, *Top. Stereochem.*, **3**, 224f (1968); (c) G. L. Closs in "Carbenes", Vol. II, R. A. Moss and M. Jones, Jr., Ed., Wiley, New York, N.Y., 1975, pp 174-183.
- (3) R. A. Moss and U-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954 (1971).
- (4) R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, **99**, 1262 (1977).
- (5) L. I. Smith and K. L. Howard, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 351.
- (6) Photolyses were run on degassed samples, sealed into Pyrex tubes, using a Rayonet reactor fitted with 3000-Å lamps. Excess diazo compound was destroyed with maleic anhydride (neither 2 nor 1 was formed during this process), and products were analyzed by GC on a 12 ft × 0.25 in., 5% Carbowax 20M column at 200 °C.
- (7) P. Yates, G. D. Abrams, M. J. Betts, and S. Goldstein, *Can. J. Chem.*, **49**, 2850 (1971).
- (8) Exact mass: calcd for $\text{C}_{17}\text{H}_{18}$, m/e 222.1408; found, 222.1410.
- (9) Control experiments established that 2 was a primary product. Photolysis of diphenyldiazomethane and 1 in 1-octene, at either 0 or -196 °C, gave no 2. Inclusion of excess benzophenone in 0 and -155 °C photolytic runs gave ratios of 2/1 of 0.268 and 6.60, respectively, not markedly different from the "normal" values; cf. Table I.
- (10) NMR analyses showed 11.1-11.2 at. % ¹³C at C₁; isobutene recovered after several photolyses showed 11.2-11.8 at. % ¹³C at this position. For preparative details, see ref 4, note 9.
- (11) Duplicate runs, at each temperature, agreed to within ±1%. NMR analyses were relative to C₆ at $\delta_{\text{C}}^{\text{TMS}}$ 22.58; analyses based on C₄ ($\delta_{\text{C}}^{\text{TMS}}$ 49.40) gave comparable results.
- (12) Reinvestigation of $\text{PhCCH}_3 + {}^{13}\text{CH}_2=\text{C}(\text{CH}_3)_2$ matrix reactions has shown the label distribution reported in ref 4 to be in serious error and the suggested addition-H migration mechanism has been withdrawn: R. A. Moss and M. A. Joyce, *J. Am. Chem. Soc.*, **99**, 7399 (1977) (correction).
- (13) In reactions of diphenylcarbene and *cis*-butene, $(E_{\text{ad}}^{\text{a,T}} - E_{\text{ad}}^{\text{a,S}}) \sim 3.6$ kcal/mol and $(E_{\text{ad}}^{\text{a,T}} - E_{\text{abst}}^{\text{a,T}}) \sim 0.9$ kcal/mol.^{1b} We assume, with Closs,^{2b} that equilibration of singlet and triplet Ph_2C is the fastest process in the system.
- (14) With Ph_2C and *cis*-butene, this value is estimated to be ≤ 2.8 kcal/mol.^{1b}
- (15) We assume that all radical pairs 3 recombine to give 2; note that little Ph_2CH_2 , which would represent escaped $\text{Ph}_2\text{CH}^\cdot$, is formed.
- (16) A similar conclusion follows if only solution data, points a-c, Figure 1, are used to determine $\Delta E_{\text{app}}^{\text{a}}$. In this case, $\Delta E_{\text{app}}^{\text{a}} = 1.5$ kcal/mol and $(E_{\text{abst}}^{\text{a,T}} - E_{\text{ad}}^{\text{a,S}}) \leq 1.5$ kcal/mol.
- (17) R. A. Moss and M. A. Joyce, unpublished work.
- (18) For examples, see H. Tomioka, T. Inagaki, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, 1023 (1976); and H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99**, 6128 (1977). The latter work, published after completion of the experiments reported herein, employs similar interpretations applied to the reactions of arylcarbenes with alcohols.
- (19) Similar conclusions follow from the work of Closs et al.^{1b}

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Selective Olefin Dimerization via Tantalocyclopentane Complexes

Sir:

We have shown recently that a neopentylidene complex, $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$, reacts with ethylene to give 4,4-dimethyl-1-pentene,¹ probably by transfer of a β -hydrogen atom selectively to the substituted α -carbon atom in an intermediate tantalocyclobutane complex.² If the organometallic product of the initial reaction, $\text{CpCl}_2\text{Ta}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)$ (1), were to decompose similarly,³ it would be a catalyst for dimerizing ethylene selectively to 1-butene, an almost unknown result for metal hydride based homogeneous catalysts.⁴ We present re-

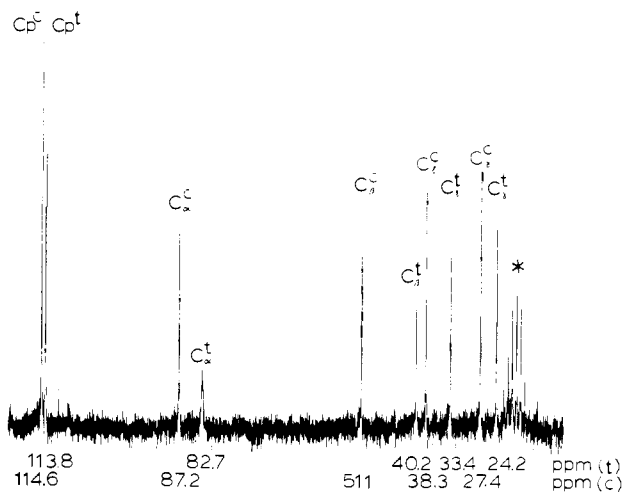
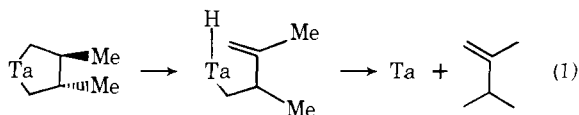


Figure 1. The 22.63-MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of a mixture of *cis*- and *trans*- $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2(\text{C}_8\text{H}_{14})$ (**3**) in toluene- d_8 (*) at 60 °C.¹⁰

sults here which demonstrate that metallocyclopentane complexes can be intermediates in selective dimerization of α olefins. They also provide some idea of the scope of such a catalytic reaction with these particular catalysts.

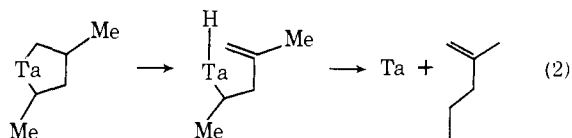
$\text{TaCpCl}_2(\text{CHCMe}_3)$ reacts with propylene in pentane at 0 °C to give 2,4,4-trimethyl-1-pentene (89%) and a thermally unstable, yellow-orange crystalline organometallic product in 70% isolated yield (**2**). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 7 °C in toluene- d_8 (Cp at 113.5, C_α at 95.6, C_β at 49.7, C_γ at 24.7) suggests that it is a β,β' -dimethyltantalocyclopentane complex analogous to **1**; the assignments are based on the multiplicity of each peak (and $^1J_{\text{CH}}$) in the gated decoupled spectrum (respectively a doublet (181 Hz), triplet (123 Hz), doublet (126 Hz), and quartet (128 Hz)). The apparent plane of symmetry (or C_2 axis) is not real, however, as shown by the ABCD pattern for the four nonequivalent protons on the $\text{C}_5\text{H}_4\text{Me}$ ring in similarly prepared ($\eta^5\text{-C}_5\text{H}_4\text{Me}$)- $\text{Cl}_2\text{TaCH}_2\text{CH}(\text{Me})\text{CH}(\text{Me})\text{CH}_2$; the methyl groups on C_β and $\text{C}_{\beta'}$ therefore must be mutually *trans* in a tetragonal pyramid (or, less likely, a trigonal bipyramid) in which C_α and $\text{C}_{\alpha'}$, C_β and $\text{C}_{\beta'}$, and C_γ and $\text{C}_{\gamma'}$ each equilibrate by "pseudorotation" on the NMR time scale.⁵ This can be confirmed by low temperature ^{13}C NMR studies; $\Delta G^\ddagger_2 \approx 12 \text{ kcal mol}^{-1}$.⁶

$\text{TaCpCl}_2(\text{C}_6\text{H}_{12})$ (**2**) is relatively stable in solution at 0 °C but decomposes rapidly at 35 °C in decane to give a 68% yield of 2,3-dimethyl-1-butene and an unidentified brown powder. In the presence of propylene 2,3-dimethyl-1-butene (93% of the product mixture) is formed *catalytically at approximately the same rate*.⁷ In both the stoichiometric and the catalytic



reaction we believe the rate-determining step to be a β -hydrogen atom shift from C_β to $\text{C}_{\alpha'}$, probably via a 3-butenyl Ta hydride complex (eq 1, Cp and Cl ligands omitted). A second primary product, 2-methyl-1-pentene (5% of the mixture), probably forms by decomposition of the thermodynamically (and/or kinetically) less favorable α,β' -dimethyltantalocyclopentane by what must be a *more favorable* transfer of the β -hydrogen atom attached to the *tertiary* β -carbon atom (eq 2). The origin of the third primary product, tetramethylethylene (2% of the mixture), is unclear at this time.⁸

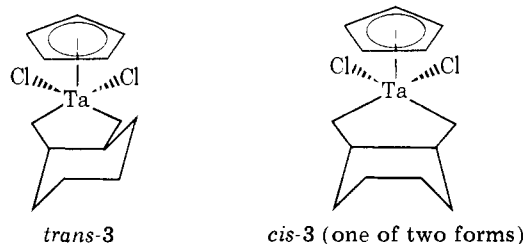
The reaction of $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ with 1-butene yields two major products. GC/mass spectral analysis suggests that one of these (59% based on Ta) is the expected "cleavage"



product, 2-ethyl-4,4-dimethyl-1-pentene (parent ion, 126; base peak, 57). The other (101% based on Ta) is a dimer of 1-butene (parent ion, 112; base peak, 55); i.e., 1-butene is dimerized stoichiometrically before the catalyst is deactivated (cf. ref 7).

$\text{TaCpCl}_2(\text{C}_4\text{H}_8)$ (**1**) is much more stable thermally than **2** but decomposes rapidly at 80 °C in mesitylene. Under 40 psig of ethylene, 1-butene is formed selectively ($\sim 3\%$ 2-butenes) and catalytically.⁹ However, two secondary products form steadily (8% after 2 h; 19% after 5 h). By GC/mass spectral analysis they both have the formula C_6H_{12} . We propose that they are ethylene/1-butene codimers formed by decomposition of a "mixed" metallocycle.

Substituted tantalocyclopentane complexes are much more stable thermally if a bicyclic system is formed. For example, $\text{TaCpCl}_2(\text{CHCMe}_3)$ reacts with 1,7-octadiene to give a pentane-soluble, orange, crystalline product with the composition $\text{TaCpCl}_2(\text{C}_8\text{H}_{14})$ (**3**) in 65% isolated yield. (Calcd: C, 36.56; H, 4.48; Cl, 16.60. Found: C, 36.20; H, 4.65; Cl, 16.69.) It can also be prepared from **1** and 1,7-octadiene. Its 22.63-MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 60 °C (Figure 1) shows it to be a mixture of complexes containing a tantalocyclopentane ring *cis* or *trans* fused to a six-membered ring, i.e., *cis*-**3** and *trans*-**3**, each of which shows only four types of ring carbons due to "pseudorotation" about Ta ($\Delta G^\ddagger_3 \approx 12 \text{ kcal mol}^{-1}$).¹⁰



Only at ~ 100 °C does **3** decompose and catalytically convert 1,7-octadiene to a complex mixture of C_8H_{14} isomers such as (we propose) α -methylmethylenecyclohexane. Studies of this and similar "internal dimerizations" (e.g., of 1,6-heptadiene) in metallocyclic complexes are in progress.

The most obvious advantage of metallocycle dimerization catalysts is the fact that isomerization of the primary product is negligible, possibly since no metal-hydride complex, except the postulated short-lived Ta^{5+} butenyl-hydride catalytic intermediate, is present.

The Ta^{5+} metallocycles are formed formally by coupling two olefins around Ta^{3+} in a " TaCpCl_2 " fragment; the redox couple is therefore $5+ \rightleftharpoons 3+$, unusually high formal oxidation states for metals involved in catalytic reactions. It is interesting in this light to find that, though $\text{NbCpCl}_2(\text{CHCMe}_3)$ ¹ does react with propylene in decane to give 2,4,4-trimethyl-1-pentene (60% yield), a paramagnetic brown powder forms concomitantly and no niobocyclopentane complex nor 2,3-dimethyl-1-butene is formed.

Acknowledgments. We thank the National Science Foundation for financial support (CHE76-07410), the Francis N. Bitter National Magnet Laboratory for use of their high-field NMR facilities, and G. Whitesides for use of his GC/mass spectroscopy facilities.

References and Notes

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- (2) The reaction of $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ with $\text{C}_6\text{H}_5\text{CH}=\text{CD}_2$ gives $\text{C}_6\text{H}_5\text{CH}=\text{CDCHCMe}_3$, consistent with this proposal.
- (3) (a) The Ti^{4+} metallocycle, $\text{TiCp}_2(\text{C}_4\text{H}_6)$, decomposes to give ethylene and 1-butene; metallocyclopentane complexes are more stable than their cyclic analogues since β -hydride elimination is suppressed, probably for steric reasons: J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *J. Am. Chem. Soc.*, **98**, 6529 (1976). (b) R. H. Grubbs, A. Miyashita, M. M. Liu, and P. L. Burk, *ibid.*, **99**, 3863 (1977).
- (4) See, for example (a) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974; (b) O. Novaro, S. Chow, and P. Magnouat, *J. Catal.*, **41**, 91 (1976); (c) G. Lefebvre and Y. Chauvin in "Aspects of Homogeneous Catalysis", Vol. 1, R. Ugo, Ed., Carlo-Manfredi Editore—Milano.
- (5) Complexes of the type $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2$ are known to be tetragonal pyramids in the solid state and often stereochemically nonrigid; see, for example, J. W. Faller and A. S. Anderson, *J. Am. Chem. Soc.*, **92**, 5852 (1970). We assume for the present that the structure and the "pseudorotation" process in complexes such as **2** are each analogous to those for the Mo complexes.
- (6) At -35°C the 67.89-MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** shows equal area peaks for C_β (51.5), C_β' (48.7), C_γ (27.2), and C_γ' (23.5); the peaks for C_α and C_α' are apparently coincident, or nearly so. For C_γ and C_γ' , $\delta\nu_\infty = 258$ Hz and $k_c = 573$ s^{-1} at $T_c \approx 258$ K or $\Delta G^\ddagger = 11.8$ kcal mol^{-1} .
- (7) The conditions are 10 mL of decane, 0.20 mmol of Ta, 45°C , and 40 psig of propylene. The initial rate (two turnovers per hour) steadily decreases as an orange, paramagnetic complex precipitates; total turnovers = 20 under these conditions. We cannot yet exclude the possibility that the catalyst is deactivated primarily by water and/or oxygen, in the propylene or solvent, or introduced when removing a sample for GC analysis.
- (8) One means by which tetramethylethylene could form is by selective decomposition of an $\alpha,\alpha,\beta,\beta$ -trimethyltantalocyclobutane formed by addition of the hydride ligand to the terminal methylene group in the butenyl-hydride intermediate, overall a ring contraction from five to four. The ratio of tetramethylethylene to 2,3-dimethyl-1-butene remains constant throughout, thus eliminating the possibility that it forms by isomerization of 2,3-dimethyl-1-butene.
- (9) Conditions are 10 mL of mesitylene and 0.20 mmol of Ta. Turnovers to 1-butene = 9.5 in 2 h, 15 in 5 h. At $t = 2$ h, the composition is 89% 1-butene, 3% 2-butenes, and 8% codimers. At $t = 5$ h, the composition is 78% 1-butene, 3% 2-butenes, and 19% codimers.
- (10) In the gated decoupled spectrum the peaks are (left to right for one isomer) a doublet for Cp, and a triplet, doublet, triplet, and triplet (with characteristic aliphatic carbon-hydrogen coupling constants) for the carbon atoms in the bicyclic ring (cf. the ^{13}C spectrum of **2**). The trans assignment is based on the fact that the C_α peak at 82.7 ppm collapses ($T_c = 273$ K at 67.89 MHz) to two peaks of approximately equal area at 96.0 and 69.1 ppm at 237 K; the cyclopentadienyl peak for neither isomer has changed at this temperature.
- (11) National Science Foundation Predoctoral Fellow, 1975–1978.
- (12) Alfred P. Sloan Foundation Fellow, 1976–1978.

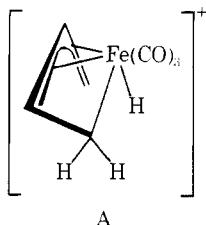
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A Novel 16-Electron Cyclooctenyliron(II) Cation

Sir:

We wish to report the first isolated and well-characterized example of the often-cited class of compounds $[\text{FeL}_3(\pi\text{-enyl})]^+$. Early work on the protonation of diene iron tricarbonyl complexes with coordinating acids was shown to give the 18-electron π -enyliron tricarbonyl halides.¹ Protonation with noncoordinating acids was originally thought to yield coordinatively unsaturated 16-electron enyliron tricarbonyl cations.² It was later shown that the isolated products were actually tetracarbonyl species with the extra carbonyl arising from partial decomposition of the starting material.³ More recently, it has been shown that the interaction of butadiene^{4,5} and cyclohexadiene⁶ iron tricarbonyl systems with strong acids gives



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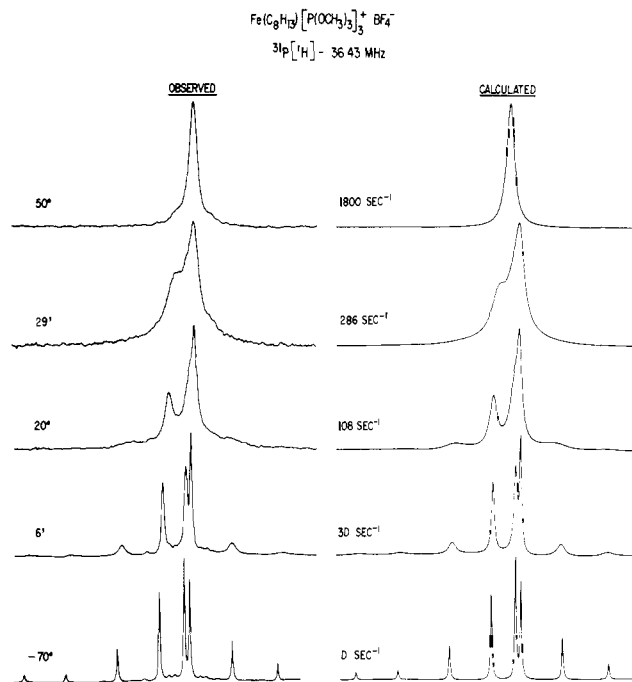
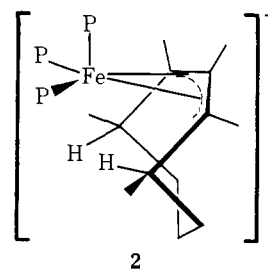


Figure 1. Observed and calculated $^{31}\text{P}\{^1\text{H}\}$ spectra for **2** as a function of temperature using an AB_2 model.

species formulated as σ - π allyl hydride complexes A. In the case of cyclohexadiene species the formulation was modified to include a three-center interaction involving the iron, hydrogen, and σ -carbon of the allyl.⁶

Protonation of $\text{Fe}(\text{P}(\text{OMe})_3)_3(\eta^4\text{-C}_8\text{H}_{12})^7$ (**1**, C_8H_{12} = 1,3-cyclooctadiene) with methanolic acids (such as HBF_4 , HCl , $\text{CF}_3\text{CO}_2\text{H}$, and $\text{CH}_3\text{CO}_2\text{H}$) gives $[\text{Fe}(\text{P}(\text{OMe})_3)_3(\eta^3\text{-C}_8\text{H}_{13})]^+$ (**2**, C_8H_{13} = cyclooctenyl), conveniently iso-



lated as the BF_4^- or BPh_4^- salts. This ease of protonation is in contrast to the strong acid systems¹⁻⁶ necessary to effect the protonation in the tricarbonyl systems. The greatly enhanced basicity of phosphite analogues of carbonyl compounds has been pointed out elsewhere.^{8,9} The field desorption mass spectrum¹⁰ gives the parent cation at mass 537. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra shown in Figure 1 indicate the fluxional nature of the complex; at room temperature the three phosphorus nuclei are equivalent; at -70°C the exchange process is frozen out, resulting in a non-first-order AB_2 spin system ($\delta_A = -173.7$, $\delta_B = -168.6$ ppm, $J_{\text{AB}} = 154$ Hz). Lowering the temperature further (to -140°C) results in no additional changes. The activation parameters for the fluxional process are $\Delta G^\ddagger_{288} = 14.4$ kcal mol^{-1} , $\Delta H^\ddagger = 16.5$ kcal mol^{-1} , and $\Delta S^\ddagger = 7.4$ cal mol^{-1} deg^{-1} .

The ^1H NMR spectrum of **2** has several unusual features. The cyclooctenyl group displays the expected allylic resonances at 5.54 (1, t)¹¹ and 5.00 ppm (2, q) and resonances attributable to eight of the aliphatic protons between 1.64 and 1.25 ppm. There is an additional resonance at -6.54 ppm (2, br q) which is assigned to protons endo to the metal (as indicated in **2**) on the carbon atom one bond removed from the allylic group. Heteronuclear decoupling experiments show no observable