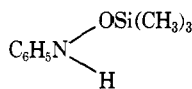


14

rotational/vibrational degrees of freedom is consistent with the negative (albeit small) ΔS^\ddagger value observed. The possible oversimplification of this interpretation is underscored, however, by noting that $\Delta S^\ddagger = -4.3$ eu for N_2 elimination from **13**. In connection with transition state considerations it is interesting that fragmentation of *O*-methyl-*N*-trimethylsilylphenylhydroxylamine^{5,11} (**2b**) in toluene at 170° to yield methoxytrimethylsilane and aniline (50% at low conversion) proceeds with a rate roughly 200 times *less* than that of **2a**. This reactivity order is opposite that predicted on purely steric grounds and is tentatively ascribed to the electropositive nature of the oxygen-bound silicon nucleus in **2a**, relative to its carbon counterpart in **2b**, which can lead to increased oxygen nucleophilicity and/or inductive stabilization of transition state **14**.

Like other reactions peculiar to organosilicon chemistry,¹³ the "driving force" for α -deoxysilylation of **2** may be reasonably associated (in part) with Si-O bond formation in **14**; especially in view of our finding that *O*-trimethylsilylphenylhydroxylamine⁵ (**15**) is essentially inert toward pyrolysis under those conditions (100° , 19 hr) which cause complete fragmentation of **2a**.



15

An additional substituent effect in the pyrolysis of **2**, akin to those manifest with **1**,^{1b} was revealed by studies with *N,O*-bis(trimethylsilyl)methylhydroxylamine¹⁴ (**2c**) in cyclohexane (*ca.* 200°) since elimination of hexamethyldisiloxane from **2c** was found to be approximately 1000 times *slower* than elimination from **2a**. While this relative reactivity order parallels that for nitrene generation from ethylazide¹⁵ and **13**,⁹ evidence for methyl-nitrene (**16**) production from **2c** is presently tenuous for it rests on our isolation of only a trace amount (1.5%) of hexamethylenetetramine together with white crystalline polymer, which are considered to be characteristic^{4b} of **16** when thermally produced under a variety of conditions. No ammonia, methylamine, or *N*-methylcyclohexylamine were detectable (vpc).

Our study of photochemically induced α -deoxysilylation of **2** has, to date, been limited to **2a** ($\lambda_{\text{max}}^{\text{C}_6\text{H}_5\text{I}_2}$ 249 m μ , log ϵ 3.88) and **2b** ($\lambda_{\text{max}}^{\text{C}_6\text{H}_5\text{I}_2}$ 247 m μ , log ϵ 3.93). Both systems undergo complete reaction within 10 min at *ca.* 35° when irradiated at 2537 Å in cyclohexane (0.005 *M*), but at this wavelength product

(10) T. B. Patrick, J. A. Schield, and D. G. Kirchner, *J. Org. Chem.*, **39**, 1758 (1974); C. Bernhart and C.-G. Wermuth, *Tetrahedron Lett.*, 2493 (1974); Y. Isowa and H. Kurita, *Bull. Chem. Soc. Jap.*, **47**, 720 (1974).

(11) Prepared (43%) by analogy to **2a** starting with *O*-methylphenylhydroxylamine.¹²

(12) W. Walter and E. Schaumann, *Justus Liebig's Ann. Chem.*, **743**, 154 (1971).

(13) C. Eaborn, "Organosilicon Compounds," Butterworth, London, 1960; L. M. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(14) O. Smrekar and U. Wannagat, *Monatsh. Chem.*, **100**, 760 (1969).

(15) G. Geiseler and W. König, *Z. Phys. Chem. (Leipzig)*, **227**, 81 (1964).

studies are complicated by extensive photodecomposition of the products, *viz.*, **6** and **12**. A comparison of thermal and photochemical reactions of **2**, together with an investigation dealing with the application of α -deoxysilylation to other group V elements will be reported in the future.

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(16) PRF-ACS Undergraduate Research Participant, 1973-1974.

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Mechanistic Studies of Oxidative Addition to Low-Valent Metal Complexes. III. Mechanism of Formation of Platinum to Carbon Bonds

Sir:

Although addition reactions of zerovalent d^{10} complexes have been extensively studied¹ and offer considerable practical utility,² few mechanistic studies are presently available.³ We present evidence that a major (but not sole) pathway for the addition of alkyl halides to the complexes $M(\text{PEt}_3)_3$ (**1**) ($M = \text{Pt}$, **1a**; $M = \text{Pd}$, **1b**)^{4,5} involves a radical chain process. Further observations on reactions of certain very reactive halides⁶ will be described in a following communication.

Despite earlier reports,⁷ addition reactions of alkyl halides with Pt^0 complexes are often quite complex. For example, excess 1-bromobutane reacts with **1a** in degassed toluene at 25° for 2 hr to produce *trans*- $\text{Pt-RBr}(\text{PEt}_3)_2$ **2a** ($R = \text{Bu}$), *trans*- $\text{PtHBr}(\text{PEt}_3)_2$ **3a**, and *trans*- $\text{PtBr}_2(\text{PEt}_3)_2$ **4a** (approximate relative yields 95:4:1), as well as small quantities ($\approx 5\%$) of butane and but-1-ene.⁸ Further reaction causes the growth of **4a**, alkene, and alkane at the expense of **2a**, while

(1) See for example (a) R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968); (b) A. J. Deeming, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci., Inorg. Chem., Series One*, **9**, 117 (1972).

(2) See M. F. Semmelhack, *Org. React.*, **19**, 115 (1972).

(3) The few mechanistic studies that have been performed generally utilize CH_3I or benzyl halides as addend, but these appear to be atypical alkyl halides. See (a) J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968); (b) K. S. Y. Lau, R. W. Fries, and J. K. Stille, *ibid.*, **96**, 4983 (1974); (c) J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, **7**, 2672 (1968); (d) R. G. Pearson and J. Rajaram, *ibid.*, **13**, 246 (1974).

(4) (a) D. H. Gerlach, A. R. Kane, G. W. Parshall, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **93**, 3543 (1971); (b) A. Musco, W. Kuran, A. Silvani, and M. W. Anker, *J. Chem. Soc., Chem. Commun.*, 938 (1973).

(5) Although most of our studies involved the very reactive **1a**, we find reactions of $\text{Pt}(\text{PPh}_3)_3$ appear to follow similar, if considerably slower, paths.

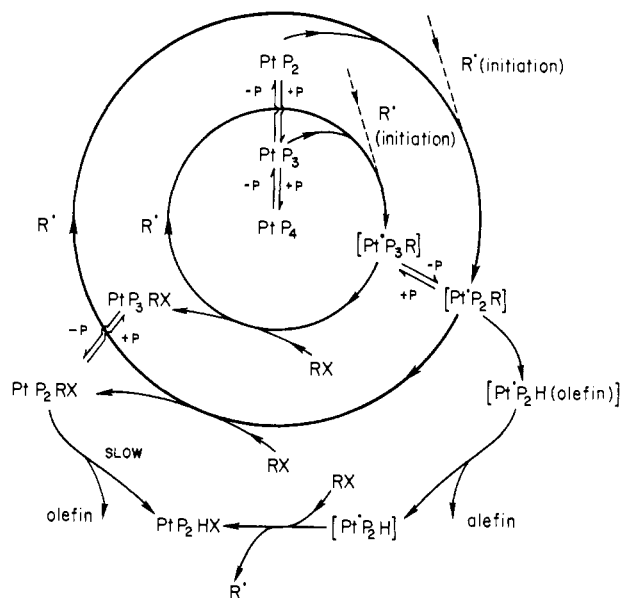
(6) A. V. Kramer and J. A. Osborn, submitted for publication in *J. Amer. Chem. Soc.*

(7) C. D. Cook and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967).

3a increases to a maximum and then decreases. Eventually the reaction products only consist of *ca.* equimolar quantities of **4a**, alkene, and alkane. The reaction of secondary alkyl bromides with **1a** generally occurs more slowly, but produces significantly larger initial quantities of **3a** at the expense of **2a**, *e.g.*, maximum yields of **2a** generally do not exceed 30–40%.

Several lines of evidence suggest that the *initial* reactions of aliphatic (and certain other related) halides with **1a** proceed as depicted in Scheme I.

Scheme I



(a) Radical scavengers (*e.g.*, 5–10 mol % of duroquinone)⁹ cause reaction rates to decrease between 5- and 10³-fold of the original rate, indicating a radical chain mechanism to be operative.

(b) In toluene the reaction of neopentyl bromide with **1a** yields not only *trans*-Pt(CH₂C(CH₃)₃)Br(PEt₃)₂ but also *trans*-Pt(CH₂C₆H₅)Br(PEt₃)₂, neopentane also being produced. When toluene-*d*₃ is used as solvent, a large isotope effect ($k_H/k_D \approx 6$) is observed for formation of the benzyl adduct. Direct hydrogen abstraction by neopentyl radicals from toluene is indicated, and, since the rate of related processes has been measured,¹¹ the rate constant¹² for capture of neopentyl radicals by Pt⁰ can be estimated as *ca.* 10 M⁻¹ sec⁻¹. Similar results are found for secondary alkyl halides, *e.g.*, cyclohexyl radicals are captured by Pt⁰ with a rate constant *ca.* 2 × 10⁻¹ M⁻¹ sec⁻¹. Unhindered pri-

(8) Reactions were generally carried out at 25° using a 0.04 M benzene and/or toluene solution of **1a** and a threefold excess of RX. ³¹P nmr (¹H noise decoupled, FT mode) data enabled monitoring of the reaction; spectra were recorded at -55° to slow phosphine exchange processes. Comparison of ³¹P nmr chemical shift and *J*^{31P-³¹P} values with authentic samples permitted unambiguous identification of all metal complexes. Note that products **3a** and **4a** are subsequently converted into the corresponding cation species, [PtH(PEt₃)₃]⁺Br⁻ and [PtBr(PEt₃)₃]⁺Br⁻ in the presence of liberated PEt₃. Alkanes and alkenes were characterized by glc.

(9) Although duroquinone forms a relatively strong π-complex¹⁰ with Pt⁰, effective scavenging still occurs. Galvinoxyl is also effective and also interacts with the complex.

(10) S. Cenini, R. Ugo, and G. LaMonica, *J. Chem. Soc. A*, 416 (1971).

(11) K. U. Ingold in "Free Radicals," Vol. I, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 2, and references therein.

(12) Note that this calculation assumes irreversible capture of the alkyl radical by Pt⁰.

mary alkyl radicals appear to be captured too rapidly for hydrogen atom transfer to compete since no benzyl products could be detected. Capture rates in excess of 10⁴ M⁻¹ sec⁻¹ are thus indicated (*vide infra*).

(c) 6-Bromohex-1-ene addition to **1a** gives an initial product ratio of *ca.* 3:1 of cyclized to linear alkyl metal adducts. Since the rate constant¹³ for closure of the 5-hexenyl radical is known (*ca.* 10⁵ sec⁻¹), the rate constant¹⁴ for capture by Pt⁰ can be estimated at *ca.* 10⁶ M⁻¹ sec⁻¹, consistent with the observations made in (b).

(d) Ethyl D-(+)-α-chloropropionate ([α]_D²⁵ +17.3°, neat)¹⁵ reacts rapidly with **1a** at 25° to yield optically inactive *trans*-Pt(CH(CH₃)COOEt)Cl(PEt₃)₂ in >95% yield. This reaction is also strongly inhibited by radical scavengers—and racemization in the radical intermediate would seem implicated.¹⁶ Note, however, the corresponding α-bromoester reacts with **1a** by a different route to yield largely **4a**.^{6,17}

(e) The general reactivity pattern for reactions of alkyl halide with **1a** is primary > secondary. The origin of this atypical ordering for a radical process is suggested by the following observations. Addition of 1 equiv of PEt₃ causes negligible inhibition of primary alkyl halide reactions with **1a**, yet effects a dramatic decrease in secondary alkyl halide reaction rates. The decrease in concentration of **1a** to form inactive Pt(PEt₃)₄¹⁸ accounts for the observed rate decrease for primary alkyl halide reactions.¹⁹ We suggest that the major path for secondary alkyl halides, however, involves the Pt(PEt₃)₂ species (*cf.* ref 3). Presumably **1a** is considerably less reactive toward hindered alkyls because of steric effects. The resultant rate order primary > secondary thus arises from [1a] ≫ [Pt(PEt₃)₂] under the usual experimental conditions.

(f) The hydride complex **3a** appears to be produced only when β-hydrogen is available on the reactant alkyl halide. The *initial* formation of **3a** in these reactions does not result from prior formation and subsequent thermal decomposition of **2a**, since we find the rate of conversion of **2a** to **3a** under these experimental conditions is too slow. We therefore suggest that β-hydrogen migration proceeds in the 15-electron species²¹ [PtP₂R]·, to yield a 17-electron intermediate

(13) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(14) This calculation assumes that cyclization occurs prior to capture by Pt⁰. We have shown that cyclization does not take place in the Pt^{II} adduct; however, the possibility of cyclization in the Pt^I intermediate cannot be ruled out.

(15) J. W. Walker, *J. Chem. Soc.*, **67**, 914 (1895).

(16) This adduct is very stable toward thermal decomposition. Further, no deuterium is incorporated into the α- and β-positions on heating in CH₃OD for several hours.

(17) Note also (a) J. A. Labinger, A. V. Kramer, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 7908 (1973); (b) S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, and K. Ataka, *ibid.*, **95**, 3180 (1973).

(18) The equilibrium constant for Pt(PEt₃)₄ ⇌ Pt(PEt₃)₃ + PEt₃ is about 0.8 M at 25°. The value for further dissociation of PEt₃ to form Pt(PEt₃)₂ has not been determined but must be considerably smaller (*cf.* ref 3 and 4a).

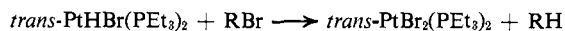
(19) Inhibition by phosphine capture of alkyl radicals to form phosphoranyl radicals can be excluded since the latter are unstable.²⁰ Further, no ethyl adducts are detected in the reaction excluding SH2 reactions by alkyl radicals on PEt₃.

(20) P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972).

(21) The electron count is the sum of the metal valence electrons and those formally donated by the ligands. For a review see C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972). Note, however, some differences between the broad generalizations of this review and the results presented herein.

[PtP₂H(olefin)]· which subsequently loses olefin, and reacts further with RX (Scheme I). β-Migration in [PtP₃R]· seems less likely since a 19-electron intermediate would be involved.²² Later in the reaction sequence, however, **3a** is predominantly formed from **2a**.

The formation of **4a** in the latter part of the reaction results from the reaction of **3a** with further alkyl halide, *i.e.*,



This process²³ is accelerated by radical initiators and a chain mechanism again appears operative. However, for some reactive halides (*e.g.*, α-bromoesters, benzyl bromide), **4a** is produced by a radical nonchain process.⁶

Although our studies on the palladium analog **1b** are less extensive, closely similar behavior is observed, *e.g.*, 5% duroquinone causes marked inhibition of additions to **1b**.

Many other organic halides do not react *via* the chain mechanism shown in Scheme I, since radical scavengers are ineffective.^{5,24} Recently a nonchain mechanism has been invoked for addition of CH₃I, C₆H₅CH₂Br, and C₂H₅I to Pt(P(C₆H₅)₃)₃ based on trapping experiments using *t*-BuNO.²⁵ Although detailed discussion must await more extensive experimental data, we find that the reaction of C₂H₅I with Pt(P(C₆H₅)₃)₃ occurs predominantly by the chain mechanism as evidenced by strong inhibition using radical scavengers, the nonchain process providing perhaps only the initiation step in this case.

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(22) Note the relative stability of the alkyl-titanium species, (π-C₅H₅)₂Ti(C₂H₅) << [(π-C₅H₅)₂Ti(C₂H₅)]⁻, may also be explained in like fashion (*i.e.*, **15e** << **17e**): H. H. Brintzinger, *J. Amer. Chem. Soc.*, **89**, 6871 (1967).

(23) Hydrogenolysis of C₆H₅CH₂Br by **3a** has been previously noted. See W. R. Moser, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. ORGN-14.

(24) No inhibition by scavengers is observed for the reaction of **1a** and **1b** with: CH₃X (X = Br, I), C₆H₅X (X = CN, Cl, Br, I), C₆H₅-CH₂X (X = Cl, Br), BrCH₂CH₂COOC₂H₅, CH₂=CHX (X = Cl, Br), *cis*- and *trans*-C₆H₅CH=CHBr, CH₂=CHCH₂X, (X = Cl, Br), and CH₂=CHCH₂CH₂Br. Inhibition is observed for: CH₃(CH₂)_nX (X = Br, I, n = 1-5), (CH₃)₂CHCH₂Br, (CH₃)₃CCH₂Br, C₆H₅(CH₂)_nBr (n = 2, 3), *c*-C₆H₁₁Br, *c*-C₅H₉Br, *c*-C₄H₇Br, *c*-C₃H₅Br, CH₃CHBr-CH₂CH₃, CH₃CHXCOOC₂H₅ (X = Cl, Br), and CH₂=CH(CH₂)₄Br.

(25) M. F. Lappert and P. W. Lednor, *J. Chem. Soc., Chem. Commun.*, 948 (1973).

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Kinetic Study of the Copper(II) Catalyzed Enolization and Decarboxylation of Oxaloacetate. Uncovering the Missing Link

Sir:

In the Cu²⁺ and Fe³⁺ catalyzed decarboxylation of α,α-dimethyl oxaloacetate, Steinberger and Westheimer found¹ that a biphasic absorbance change occurs

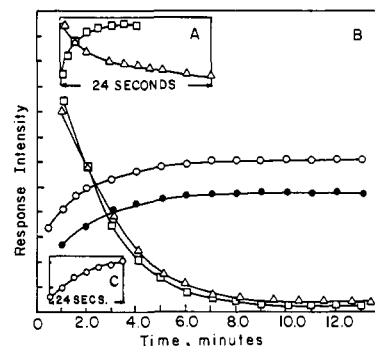
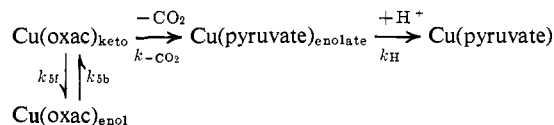


Figure 1. Response-time curves for the decarboxylation and enolization of Cu(II) oxaloacetate: ○, manometric CO₂ evolution; ●, H⁺ ion consumption by pH stat (pH 3.19); □, absorbance change at 514 nm (in the absence of Methyl Orange); △, absorbance change at 514 nm of the acid form of Methyl Orange; Cu(II)_{tot} = 0.025 M; oxac_{tot} = 0.0071 M; pH_{init} 3.4; pH_{final} 4.2; 25°.

in the near-uv region. This was attributed to the formation of a highly absorbing derivative of pyruvate enolate which then undergoes protonation and ketonization to yield the low absorbing ketone. A similar sequence of absorbance changes which occur on mixing metal ion and oxaloacetate (oxac²⁻) solutions has been interpreted in terms of either the Steinberger-Westheimer mechanism² or to the preequilibrium formation of absorbing oxac²⁻ enol complexes which are depleted as decarboxylation proceeds. In this latter sequence the intermediate pyruvate enolate is considered to be too transient to be observed.^{3,4} Recent quantitative results from these laboratories for the Zn²⁺-oxac²⁻ systems⁵ favor the latter interpretation; however, a comprehensive set of experiments described here shows that the Cu(II) catalyzed reaction is considerably more complicated than heretofore reported and exhibits the features of both of these mechanisms.

The reaction scheme which applies to this system involves the following steps



We have found that the release of CO₂ is biphasic as is also the rate of H⁺ uptake in the step where pyruvate is formed. These characteristics enable sufficient information to be obtained to determine the individual rate constants.

On mixing buffered oxac²⁻ and Cu²⁺ solutions, three relaxations can be identified in time ranges greater than 1 sec. These are shown in Figure 1. The fastest of these relaxations (τ₁) produces an absorbance increase at 320 nm which is complete within 30 sec. This is followed by an absorbance decrease which requires up to 30 min for completion (τ₃). These two processes

(1) R. Steinberger and F. H. Westheimer, *J. Amer. Chem. Soc.*, **73**, 429 (1951).

(2) E. Gelles and R. W. Hay, *J. Chem. Soc.*, 3673 (1958).

(3) A. Kornberg, S. Ochoa, and A. Mehler, *J. Biol. Chem.*, **174**, 159 (1948).

(4) E. Bamann and V. S. Sethi, *Arch. Pharm. (Weinheim)*, **301**, 78 (1968).

(5) W. D. Covey and D. L. Leussing, *J. Amer. Chem. Soc.*, **96**, 3860 (1974).