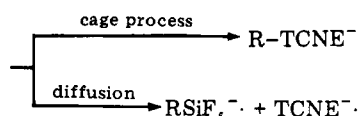The ESR monitoring of the reaction mixture revealed, if qualitatively, that TCNE anion radicals appeared to be accumulated as the reaction proceeded. These facts strongly suggest that the present reaction proceeds by an initial one-electron transfer from silicate to TCNE (route A) rather than a direct electrophilic alkyl transfer (route B), and that there may be some leakage of radical species from the cage.
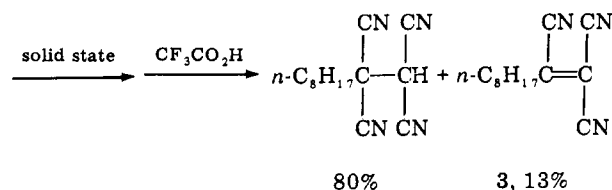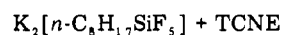
Although kinetic data were not available, the relative reactivities of alkylpentafluorosilicates shown in Table I provide further support for the electron-transfer mechanism. While the methylsilicate failed to react with TCNE probably because of the low electron-donating ability of the methyl group, cyclohexyl- and 2-norbornylsilicates reacted in spite of steric hindrance. These facts are also consistent with the electron-transfer mechanism in which the electron-donating ability of an alkyl group is more important than steric factors.[4b]

The following observation is also worth noting. In the reaction of *exo*-2-norbornylpentafluorosilicate[1] with TCNE a 1:1 mixture of *exo*- and *endo*-(2-norbornyl)-1,1,2,2-tetracyanoethane[9] was formed, whereas from *endo*-2-norbornylsilicate[1] only one isomer of the alkylation products was obtained, which was identified as the exo isomer by its ^{1}H NMR spectrum.[10] This stereochemical result[12] suggests a partial diffusion of the norbornyl radical from a cage arising from the exo silicate. In the main reaction course, there must be some inter-

$$RSiF_s{}^{2-} + TCNE \longrightarrow [RSiF_s{}^{-}\cdot,\ TCNE^{-}\cdot]$$

$$\begin{array}{c} \text{cage process} \longrightarrow R\text{–}TCNE^{-} \\ \text{diffusion} \longrightarrow RSiF_s{}^{-}\cdot + TCNE^{-}\cdot \end{array}$$

action between carbon and silicon atoms during the transfer of an alkyl group to the TCNE anion radical or TCNE. Alkyl transfer may occur not only within a cage, but also after diffusion of radical species.[13]

Similar alkylation reactions also took place in the solid state. Mixing of powdered octylpentafluorosilicate and TCNE under vacuum resulted in a violet mixture which showed intense ESR absorptions due to the TCNE anion radical.[14] Stirring the solid mixture at 3 °C for 8 h, followed by quenching with trifluoroacetic acid, afforded 1,1,2,2-tetracyanodecane (1, R = C_8H_{17}) and 1,1,2-tricyano-1-decene (3) in 80 and 13% yields, respectively. The latter is considered to be formed by elimi-

$$K_2[n\text{-}C_8H_{17}SiF_5] + TCNE$$

$$\xrightarrow[\text{CF}_3\text{CO}_2\text{H}]{\text{solid state}} n\text{-}C_8H_{17}\overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}\text{---}\overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle CN}{|}}{CH}} + n\text{-}C_8H_{17}\overset{\overset{\displaystyle CN}{|}}{C}{=}\overset{\overset{\displaystyle CN}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}$$

$$\qquad\qquad 80\%\qquad\qquad 3,\ 13\%$$

nation of hydrogen cyanide from the cyanocarbanion intermediate 2 under reduced pressure.[4a] The successful electron-transfer reaction in the solid state indicates that an electron-transfer process can occur at the solid surface of organopentafluorosilicates.

In conclusion the reaction of organopentafluorosilicates with TCNE proceeds through an initial one-electron transfer. The ease of one-electron release from organopentafluorosilicates suggests their relatively low ionization potentials and the possibility that their reactions with other oxidizing agents may also involve such an electron-transfer process. Further mechanistic studies are now in progress.

References and Notes

(1) Organofluorosilicate in organic synthesis. 10. For part 9, see Tamao, K.; Yoshida, J.; Murata, M.; Kumada, M. *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) For example: (a) Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351. (b) Kochi, J. K. "Organometallic Mechanism and Catalysis"; Academic Press: New York, 1978; Chapters 15 and 16.
(3) (a) Mueller, R. *Organomet. Chem. Rev.* **1966**, *1*, 359. (b) Tamao, K.; Yoshida, J.; Takahashi, M.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Kurita, A.; Kumada, M. *J. Am. Chem. Soc.* **1978**, *100*, 290. (c) Tamao, K.; Kakui, T.; Kumada, M. *Ibid.* **1978**, *100*, 2268. (d) Yoshida, J.; Tamao, K.; Kurita, A.; Kumada, M. *Tetrahedron Lett.* **1978**, 1809.
(4) Reactions of other organometallic compounds with TCNE have been studied extensively: (a) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 558. (b) Gardner, H. C.; Kochi, J. K. *Ibid.* **1976**, *98*, 2460. (c) Chaudhury, N.; Kekre, M. G.; Puddephatt, R. J. *J. Organomet. Chem.* **1974**, *73*, C17. (d) Su, S. R.; Wojcicki, A. *Ibid.* **1970**, *21*, 21. (e) Su, S. R.; Wojcicki, A. *Ibid.* **1971**, *31*, C34. (f) Su, S. R.; Wojcicki, A. *Inorg. Chem.* **1975**, *14*, 89. (g) Hartman, G. D.; Traylor, T. G. *Tetrahedron Lett.* **1975**, 939.
(5) Allyltrimethylsilane has been reported to react with TCNE to form 4,4,5,5-tetracyano-1-pentene after hydrolysis.[4g]
(6) $n^{20}{}_D$ 1.4585; ^{1}H NMR (CDCl₃, Me₄Si) δ 0.90 (t, J = 6 Hz, 3 H), 1.1–2.0 (m, 12 H), 2.1–2.4 (m, 2 H), 4.45 (s, 1 H) ppm; ^{13}C NMR (CDCl₃, Me₄Si) δ 110.68 (s), 107.37 (s), 39.59 (s), 35.82 (t), 31.64 (t), 31.59 (d), 28.91 (t, t), 28.42 (t), 25.64 (t), 22.57 (t), 14.02 (q) ppm; MS (24 eV) *m/e* (%) 215 (M⁺ − HCN, 1), 214 (2), 200 (7), 186 (25), 172 (28), 159 (22), 158 (17), 145 (18), 144 (11), 117 (31), 69 (11), 57 (100), 43 (98), 41 (27); IR (neat) 2925 (s), 2855 (m), 2265 (vw), 1415 (s), 1376 (w), 895 (w), 758 (m), 738 (m), 721 cm⁻¹ (w). Calcd for $C_{14}H_{18}N_4$: C, 69.39; H, 7.49; N, 23.12. Found: C, 69.52; H, 7.55; N, 23.21. Similar alkylation products have been obtained by the reaction of TCNE with Grignard reagents and other metal alkyls.[4a,b]
(7) All products exhibited consistent ^{1}H NMR, IR, and MS spectra and elemental analysis.
(8) ESR parameters for TCNE anion radical generated by reduction with potassium metal in 2-methyltetrahydrofuran were a_N = 0.157₂ mT and g = 2.0027₉.
(9) Determined by comparison of intensities of ^{1}H NMR (100 MHz) signals of the methine proton –C(CN)₂H. These methine signals arising from two stereoisomers occur as a very close doublet around 4.4 ppm in CDCl₃, but shift upfield and separate sufficiently so that the intensities in a mixture of benzene and CDCl₃ containing a small amount of trifluoroacetic acid can be measured.
(10) Only one methine proton –C(CN)₂H was observed by ^{1}H NMR and it was identified as the exo isomer by the inspection of the spin coupling pattern of the norbornyl 2-methine proton[11] (δ 2.25 ppm, br t, J = 6.8 Hz).
(11) Flautt, T. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 3212.
(12) Similar stereochemical phenomena have been observed for the bromine cleavage of *exo*- and *endo*-2-norbornylsilicate.[1]
(13) The latter step may be followed by several radical chain processes which are consistent with all of the present observations, e.g.,

$$RSiF_5{}^-\cdot + TCNE \rightarrow R\text{–}TCNE\cdot + SiF_5{}^-$$
$$R\text{–}TCNE\cdot + RSiF_5{}^{2-} \rightarrow R\text{–}TCNE^- + RSiF_5{}^-\cdot$$
$$RSiF_5{}^-\cdot \rightarrow R\cdot + SiF_5{}^-$$
$$R\cdot + TCNE \rightarrow R\text{–}TCNE\cdot$$

We thank one of the referees for suggestions of radical chain mechanisms.
(14) The ESR spectrum of the solid mixture measured at 77 K coincides with that of a frozen 2-methyltetrahydrofuran solution of potassium tetracyanoethylenide observed at 77 K.

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Titanium-Mediated Methylene-Transfer Reactions. Direct Conversion of Esters into Vinyl Ethers
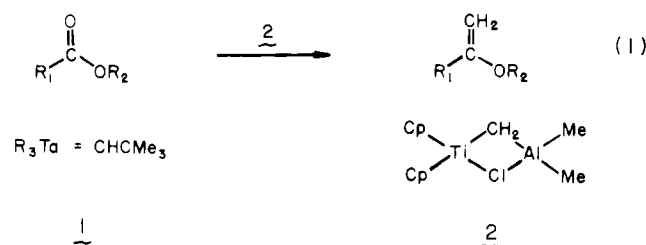
Sir:

To date, the direct methylenation of esters (eq 1) via phosphorus ylides has not proven to be a generally viable synthetic operation.[1,2] However, recent studies by Schrock[3] and Tebbe[4] show that the more electrophilic "transition metal ylides" such

Table I. Representative Reactions of Esters With Cp₂TiCH₂AlClMe₂ (2)

Entry	Substrate	Product[a]	Yield, %[b]
A	Ph–C(O)–OR	PhC(CH₂)–OR R = Ph	94 (≥95)
		R = Me	81 (≥95)
B	PhCH₂–C(O)–OEt	PhCH₂–C(CH₂)–OEt	90 (98)
C	(structure) CH₃ ketal –OEt	(structure) CH₂ –OEt	87
D	(benzofuranone)	(methylene benzofuran) CH₂	85
E	(chromanone)	(methylene chroman) CH₂	85
F	Ph (keto ester) OEt **3**	Ph CH₂ OEt CH₂	97
G	Ph–CH₂–C(O)–O–(cyclohexenyl)	Ph–CH₂–C(CH₂)–O–(cyclohexenyl)	96

a All products afforded satisfactory IR, NMR, and mass spectra.
b Yields cited are on isolated and purified olefinic products. Yields reported in parenthesis were determined by NMR.

$$R_1-\overset{\overset{\text{O}}{\|}}{C}-OR_2 \quad \xrightarrow{\ 2\ } \quad R_1-\overset{\overset{\text{CH}_2}{\|}}{C}-OR_2 \qquad (1)$$

$R_3Ta = CHCMe_3$

1   **2**

as 1 and 2 can be used to effect alkylidene transfer to carboxylic acid derivatives. For example, Tebbe reported that 2 reacted with ethyl acetate to give ethyl isopropenyl ether. The purpose of this communication is to disclose our observations on the use of the titanium complex 2 for a wide range of ester and lactone methylenations.

The solid complex 2[5] was synthesized according to the procedure described by Tebbe and co-workers.[4] Because of the general sensitivity of 2 to both air and moisture, handling of the complex was facilitated by employing standardized solutions[5] of the complex in either benzene or toluene (~0.5 M). Although the limiting shelf life of these solutions has not been determined, no loss in "active reagent titer" was observed over a 2-month period at room temperature. In a typical experiment, 1.0 mmol of ester is dissolved in 2 mL of toluene–THF (3:1) and 10 μL of pyridine and cooled to −40 °C. A solution of 1.1 mmol of 2 in toluene (0.55 M) is added dropwise (1–3 min) and the reaction is maintained at −40 °C for 0.5 h and then allowed to warm to ambient temperature over an additional 90-min period. The reaction is quenched by the dropwise addition of 0.3 mL of 15% aqueous sodium hydroxide solution to the cooled (ca. −10 °C) reaction mixture and allowed to warm to room temperature. After gas evolution has ceased, the

Table II. Representative Reactions of Unsaturated Esters with Cp₂TiCH₂AlClMe₂ (2)

| Entry	Substrate	Product[a]	Yield, %[b]
A	R (unsat ester) OEt	R OEt CH₂ R = Me	82
		R = Ph	96
B	Ph (structure) OMe **c**	Ph CH₂ OMe **d**	79
C	EtO (diene keto ester)	EtO CH₂ (diene)	81

a,b See footnotes *a* and *b*, Table I. *c* See N. Takamura, T. Mizoguchi, and S. Yamada, *Chem. Pharm. Bull.* (*Jpn.*), **23**, 299 (1975), for synthesis. In our hands this procedure afforded the *Z* olefin contaminated by ≤10% *E* isomer. *d* The *Z:E* isomer ratio was ≥90:10.

dark green solution is diluted with excess ether, dried with sodium sulfate, and filtered through a Celite pad. Upon solvent removal in vacuo the crude vinyl ether may be purified by filtration through a short column of alumina (neutral, activity III) employing hexane as an eluant. In all cases, the methylenation product was the only compound observed on solvent removal. The list of representative esters employed in this study are illustrated in Tables I and II. In those instances where bis methylenation was desired (Table I, entry F; Table II, entry C) solvent volumes and reagent quantities were doubled. We have observed that the overall reaction rate is dramatically affected by the presence of donor ligands (THF, C₆H₅N). For example, equimolar quantities of methyl benzoate and 2 in toluene (~0.3 M) require times of 24 h (25 °C) for complete reaction; however, upon the addition of either THF or pyridine complete methylenation was observed within 1 h at 25 °C. Related observations pertaining to the effect of Lewis bases on the reactivity of 2 toward olefins have been noted.[4]

Inspection of Table I reveals that the reaction of the Tebbe reagent 2 with a variety of substrates is a general, high-yield synthetic operation which will tolerate both ketal and olefin functionality. Entries B, D, and G illustrate the important point that olefin positional integrity is maintained throughout the reaction. No evidence was found for *any* olefin isomerization in any of these reactions. Keto ester 3 (entry F) illustrates the point that ketone as well as ester methylenation is possible. With this substrate competition experiments revealed that the rate of ketone methylenation was approximately four times that of ester methylenation.

The direct transformation of α,β-unsaturated esters of 2-alkoxy dienes was also examined. As summarized in Table II, the presence of a conjugated olefin does not interfere with the carbonyl methylenation process. Both *E* and *Z* cinnamate esters are transformed to the corresponding dienes *without* loss of stereochemistry.

The ester methylenation procedure outlined in this study provides a useful extension to the methods currently available for the construction of allyl vinyl ethers which are valuable as substrates for the Claisen rearrangement (eq 2). In addition,

$$(2)$$
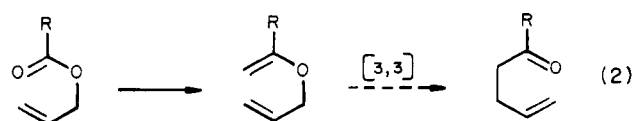
complex alkoxy-substituted dienes, not readily synthesized by conventional methods, should prove useful in intramolecular

(3)
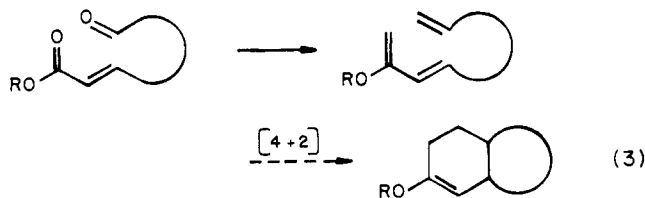
Diels–Alder reactions (eq 3). Related reactions with other carboxylic acid derivatives will be reported in due course.

References and Notes

(1) A. P. Uijttewaal, F. L. Jonkers, and A. van der Gen, *J. Org. Chem.*, **44**, 3157 (1979).
(2) For studies related to this synthetic operation, see M. LeCorre, *Bull. Soc. Chim. Fr.*, **9–10**, 2005 (1974); H. J. Bestmann, K. Rostock, and H. Dornauer, *Angew. Chem.*, **78**, 335 (1966); H. J. Bestmann, H. Dornauer, and K. Rostock, *Chem. Ber.*, **103**, 2011 (1970).
(3) R. R. Schrock, *J. Am. Chem. Soc.*, **98**, 5399 (1976).
(4) F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, **100**, 3611 (1978).
(5) The purity of **2** was assayed by ^{1}H NMR (C_6D_6) using a toluene internal standard and was obtained in a state of purity of 75% (by weight).[4] Toluene solutions of **2** under argon were prepared and assigned a "titer value" based upon the above ^{1}H NMR assay. Standardization of solution of **1** was also carried out by allowing a measured volume of the above solution to react with a measured quantity of methyl benzoate in an NMR tube under argon. Assuming a 1:1-reaction stoichiometry, the titer determined by this method was in agreement with the state of purity of the solid complex as ascertained by ^{1}H NMR.
(6) On sabbatical leave from the Department of Chemistry, California State University, Los Angeles, Calif.
(7) National Institutes of Health Postdoctoral Fellow.

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Can Chemical Reactivity Patterns on Chemically Modified Electrode Surfaces Be Anticipated from Solution Reactivity? A Study of Ruthenium Nitro Complexes

Sir:

Recent work[1] has shown that monolayers of electron-transfer couples immobilized on electrode surfaces via organosilane reagents undergo rapid electron transfer to and from the electrode. Such observations point to the possibility of linking homogeneous redox catalysis to heterogeneous electrocatalysis, by attaching reactive homogeneous catalysts to electrodes. Advantages gained would include the small amount of catalyst required, ready separability of products, and an electrode-controlled turnover rate. Central to this possibility is whether reactivity patterns of the homogeneous catalyst are preserved or usefully modified by its attachment to the electrode.

We have investigated the reactivity of immobilized ruthenium 2,2′-bipyridine (bpy) complexes which contain nitro or nitrosyl ligands and whose homogeneous chemistry[2,3] includes an example of oxidative catalysis.[3] Immobilization of the ruthenium nitro complex was achieved by silylamine functionalization of a Pt electrode[1a] surface (eq 1), followed by amide coupling[4] (eq 2). The $Ru^{II}NO_2$ electrodes I exhibit an electrochemical oxidation wave at $E_{peak,anod} = +1.08$ V vs.
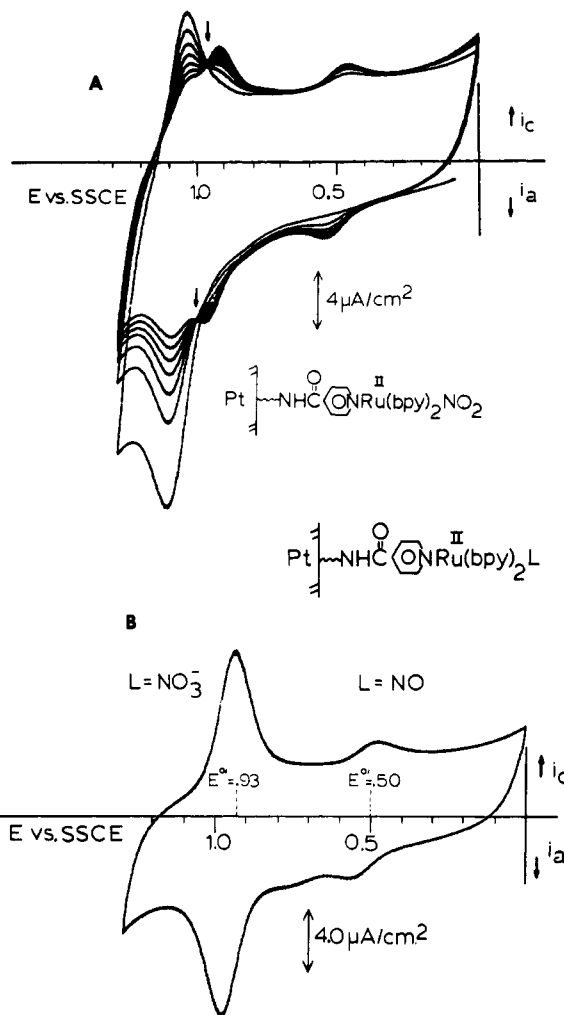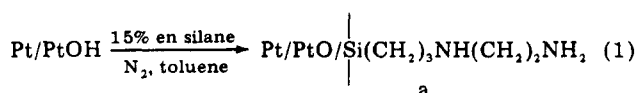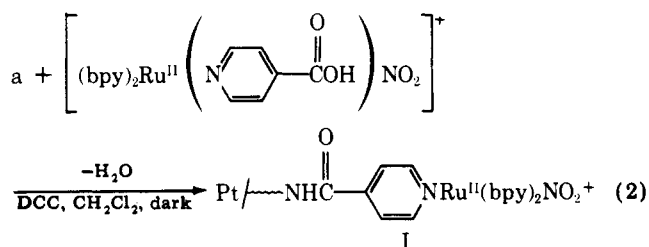
$$Pt/PtOH \xrightarrow[\text{N}_2,\text{ toluene}]{\text{15\% en silane}} Pt/PtO/\underset{\underset{\text{a}}{|}}{\overset{|}{Si}}(CH_2)_3NH(CH_2)_2NH_2 \quad (1)$$

Figure 1. Cyclic voltammetry of I in 0.1 M $Et_4N^+ClO_4$–acetonitrile at 0.2 V/s. Current sensitivity, $4\mu A/cm^2$. Curve A: first seven cyclical potential scans. Arrows denote isopotential points. Curve B: after 40 scans (i.e., after disproportionation).

SSCE in acetonitrile attributable to oxidation of (typically) 1×10^{-10} mol/cm^2 of I (eq 3).
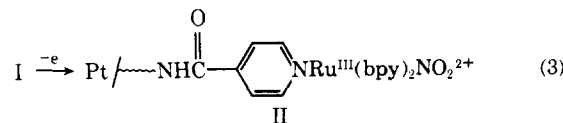
Oxidation of the homogeneous solution analogue, [(bpy)$_2$-Ru^{II}(py)NO$_2$]$^+$, occurs at $E_{peak,anod} = +1.06$ V vs. SSCE in acetonitrile, but the Ru^{III}NO$_2$ complex, [(bpy)$_2$Ru^{III}(py)-NO$_2$]$^{2+}$, once formed is unstable and undergoes a net disproportionation at the nitro ligand[2a,b] (eq 4). Following oxidation, reversible cyclic voltammetric waves appear for the nitrato [(bpy)$_2$Ru(py)ONO$_2$]$^{2+/+}$ and nitrosyl [(bpy)$_2$Ru(py)-NO]$^{3+/2+}$ complexes at $E^{o\prime} = +0.91$ and $+0.53$ V vs. SSCE, respectively.