Multiple Temperature Electrochemical Studies of the Oxidatively Catalyzed *E*–*Z* Isomerization Reactions in Iron Alkenyl Complexes. Improved Resolution of Closely Spaced Redox Systems Using Deconvolution Voltammetry

Robert H. Philp, Jr.,* and Daniel L. Reger

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Alan M. Bond

Department of Chemical and Analytical Sciences, Deakin University, Geelong, Victoria 3217, Australia

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The one-electron electrochemical oxidation of the eighteen-electron (18e) Z and E isomers of CpFeCO[P(OPh)$_3$](η^1-C(Ph)=C(Ph)Me) to their seventeen-electron (17e) counterparts has been studied by cyclic voltammetry and by deconvolution (semidifferential) voltammetry in dichloromethane in the temperature range −87 to 22 °C. At room temperature the 17e cations appear to be unstable and the electrochemistry is that of an EC system with a half-life of 0.4 s. At temperatures below ca. −60 °C two reversible redox couples are resolved in mixtures, whereas at temperatures around −20 °C the electrochemical response is indistinguishable from that of a single simple reversible system. This is attributable to the temperature dependent, but rapid E^+ to Z^+ isomerization and associated cross redox reaction. The electrochemistry at −78 °C may be described by the following equations:

$$Z \rightleftharpoons Z^+ + e^- \quad E_{1/2} = 0.51 \text{ V vs Ag/AgCl}$$

$$E \rightleftharpoons E^+ + e^- \quad E_{1/2} = 0.65 \text{ V vs Ag/AgCl}$$

$$E^+ \xrightarrow{\text{fast}} Z^+$$

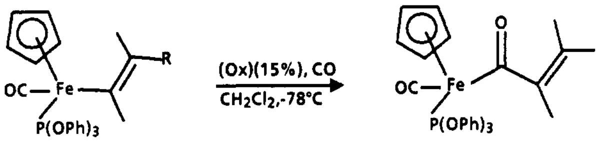
$$E^+ + Z \rightleftharpoons Z^+ + E \quad K_{eq} = 4 \times 10^3$$

By combining the $E_{1/2}$ values measured at low temperature with NMR data for the neutral species an equilibrium ratio [CpFeCO[P(OPh)$_3$](η^1-(Z)-C(Ph)=C(Ph)Me)]$^+$/[CpFeCO[P(OPh)$_3$](η^1-(E)-C(Ph)=CMe(Ph)]$^+$ of 9×10^2 at −78 °C is calculated. In the 18e configuration the E rather than the Z isomer is favored by a factor of about 5:1 so the isomer distribution is strongly modified by oxidation to the 17e configuration. The change in isomer distribution may have implications in the synthetic chemistry of this class of compounds.

Introduction

Electrochemical data, especially when coupled with spectroscopic results, continue to be of great value in providing insight into structure and reactivity in organometallic systems. Of considerable recent interest have been studies designed to elucidate the enhanced reactivity of 17-electron (17e) relative to 18-electron (18e) organometallic species in migratory insertion and in ligand substitution reactions.[1-8]

Alkenyliron complexes are compounds for which interesting and useful synthetic chemistry is being developed.[9,10] Synthetic and structural studies[10] have demonstrated that a number of alkenyliron complexes react rapidly with CO (1 atm) at −78 °C in the presence of catalytic amounts of chemical oxidant (Cp$_2$Fe$^+$ or Ce^{4+}) to yield alkenylacyl complexes (eq 1). These reactions do not take place in the absence of the oxidizing reagent. Although generally the reaction proceeds with retention of alkenyl stereochemistry, in certain cases where a phenyl group is trans to iron, inversion of stereochemistry to the cis form is observed (eq 2).



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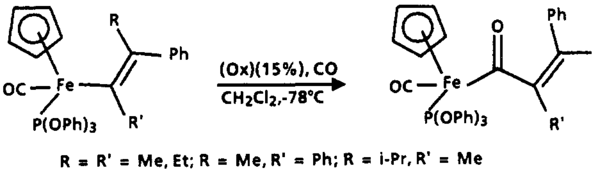

(2)

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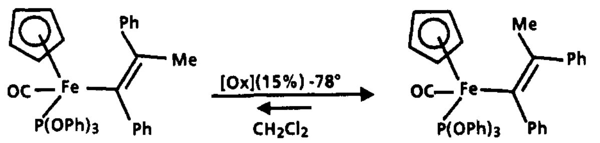
In the absence of CO, the isomerization of the alkenyl ligand is also catalyzed by oxidizing reagents as shown in eq 3. For the example shown in eq 3, NMR measurement



(3)

Z **E**

shows that the equilibrium mixture is a 1:4.7 ratio of the *Z* to *E* isomers. This isomerization reaction does *not* take place thermally, but it is also catalyzed by acids and Al_2O_3.

This work describes an electrochemical study in dichloromethane of the equilibrium reaction shown in eq 3 undertaken in order to determine, if possible, the difference in oxidation potential of the two alkenyl isomers, to establish the relative thermodynamic stability of the two 17e species produced by a one-electron oxidation process, and ultimately to gain a better understanding of factors influencing reactivity and product distribution in oxidatively induced insertion of CO in alkenyliron complexes. The systems chosen for study were various mixtures of *Z* and *E* isomers of $CpFeCO[P(OPh)_3](\eta^1\text{-}C(Ph){=}C(Ph)Me)$. Specifically, we have examined a pure sample of the *Z* isomer (designated *Z*), an equilibrium mixture of *E* and *Z* ($[E]/[Z] = 4.7$ at −78 °C; designated *E*/*Z*), and a nonequilibrium mixture, approximately 70% *Z* (designated *Z* + *E*) which was prepared by stirring a pure *Z* sample for about 5 min in a suspension of Al_2O_3 in CH_2Cl_2.

It should be noted that the electrochemical response in systems of interconverting isomers is a matter of considerable complexity.[11,12] A wide variety of behavior may be observed, depending upon the thermodynamic and kinetic factors governing the relevant heterogeneous and homogeneous reactions. As an example, it was recently shown[13] that equilibrium and nonequilibrium mixtures of *cis*- and *trans*-$Cr(CO)_4(P[OMe]_3)_2$ exhibit oxidative cyclic voltammetric (CV) behavior indistinguishable from that of a simple reversible one-electron system even at scan rates (v) of 5×10^4 V/s at microelectrodes. This is in spite of the fact that calculations from spectroscopic data show that a resolvable difference in reversible half-wave potential ($E_{1/2}$) for the two isomers is expected.

Experimental Section

The synthesis, purification, and NMR analysis of (*Z*)- and (*E*)-$CpFeCO[P(OPh)_3](\eta^1\text{-}C(Ph){=}C(Ph)Me)$ were carried out as previously reported.[10]

Electrochemical Studies. The dichloromethane solvent was HPLC grade and distilled from CaH_2 just prior to use. Vaccum-dried tetrabutylammonium hexafluorophosphate ($TBAPF_6$) from Southwestern Analytical Chemicals was employed as the supporting electrolyte.

A standard three-electrode cell was employed. The reference electrode was Ag/AgCl (CH_2Cl_2; saturated LiCl, 0.10 M tetrabutylammonium perchlorate) separated from the test solution by a salt bridge containing 0.10 M $TBAPF_6$. A conventional gold disk working electrode was used. All measurements were made under an Ar atmosphere in a cell protected from light. Solutions were prepared by transferring weighed samples of the compounds to the cell containing a degassed solution of the supporting electrolyte. Low temperatures were produced by use of liquid N_2 slushes with acetone (−87 °C), chloroform (−63 °C), and carbon tetrachloride (−23 °C) and monitored with a calibrated thermocouple.

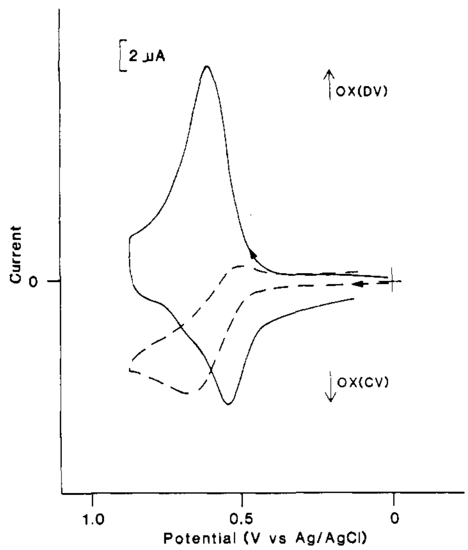


Figure 1. CV and DV curves for *Z* + *E* (1.1 mM) at 22 °C (v = 600 mV/s).

Preliminary cyclic voltammetric (CV), differential pulse (DP), and rotating disk (RDE) measurements were made by using a PAR Model 174 polarographic analyzer along with a Metrohm rotating disk electrode assembly. All of the deconvolution voltammetric (DV) curves and most of the CV measurements presented in this paper were obtained by using the BAS CV-27 system. This instrument provides the semiderivative of the current as an output option, and this signal was recorded directly.

Results and Discussion

Deconvolution Voltammetry. In this study we found measurement of the semiderivative of the current upon application of a potential ramp to the electrode to be far superior to CV in the resolution of the closely spaced electrode processes. This technique, first reported by Goto and Ishii[14] and developed by Oldham and co-workers,[15,16] provides, by appropriate processing of the current, a symmetrical peaked response (the semiderivative, *e*, vs applied potential) in place of the conventional CV curve. It has the obvious advantages of a differential response on the time scale of CV. The term deconvolution voltammetry (DV) has been suggested as appropriate for the technique.[17] Using ferrocene in CH_2Cl_2 as a model system we verified conformance to the DV curve parameters predicted for an uncomplicated system.[16] While theory predicts no difference in anodic and cathodic peak potentials, a small separation (ΔE_p) was noted due to uncompensated resistance (ohmic *iR* drop), particularly at low supporting electrolyte concentrations and low temperature. The $E_{1/2}$ value ($\simeq E^\circ$) taken as the mean of the anodic and cathodic DV peak potentials was, however, exactly the same as that calculated from the mean of the CV peak potentials and was completely invariant with scan rate, v.

In the discussion to follow, unless otherwise noted, all anodic and cathodic peak potentials ($E_p^{ox.}$ and $E_p^{red.}$) and peak currents ($i_p^{ox.}$ and $i_p^{red.}$) will be from DV data.

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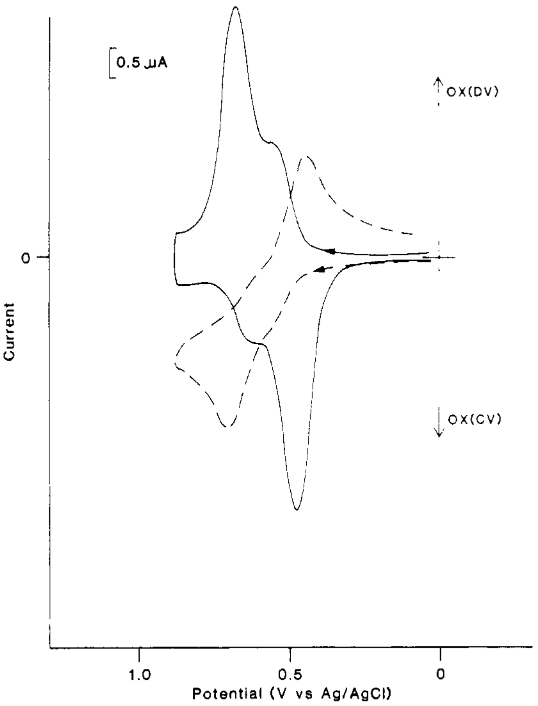

Figure 2. CV and DV curves for *E*/*Z* (0.5 mM) at −87 °C (v = 400 mV/s).

Alkenyliron Complexes. At room temperature (22 °C) all systems examined exhibit the same electrochemical response, shown in Figure 1. This is despite the fact that the mixtures are spectroscopically distinguishable (NMR). (It should be noted that in all figures the CV oxidation currents are plotted downward while the DV oxidation currents are plotted upward.) Features ($E_{3/4} - E_{1/4}$; $i_L/C\omega^{1/2}$) of RDE curves for this oxidation, as compared to ferrocene are entirely consistent with an electrochemically reversible one-electron process. ($E_{3/4}$ and $E_{1/4}$ are potentials at $^1/_4$ and $^3/_4$ of the limiting current i_L; C is concentration; ω is rotation rate.) However, unlike ferrocene the system shows a degree of chemical irreversibility such that a half-life ($t_{1/2}$) of 0.4 s (0.7 s at 10 °C) is calculated[18] at 22 °C from peak current ratios as a function of v for the unidentified decomposition reaction of the 17e species.

A second oxidation is observed with both isomers at 1.05 V which also shows a high degree of chemical reversibility at room temperature. This process was not further investigated.

At −87 °C a solution of the equilibrium mixture (*E*/*Z*) exhibits the CV and DV responses shown in Figure 2. Here, unlike the case at room temperature, two oxidation processes are clearly visible in the DV scan and indicated, but much less evident, in the CV data. The total current corresponds to a one-electron process. The ratio of the DV peak currents of the partially resolved oxidation peak at 0.55 V (least positive) to that of the principal peak at 0.68 V (more positive) is in reasonable agreement with the ratio of *Z* to *E* in the equilibrium mixture as determined by NMR. However, it should be particularly noted in Figure 2 that the reduction DV peak at 0.47 V on the reverse scan exhibits a peak current more than twice that of the corresponding oxidation peak at 0.55 V and is, in fact, closer in height to the second oxidation peak at 0.68 V. This clearly indicates that the product of the oxidation at 0.68 V is rapidly converting to the species which is reduced at 0.47 V, even at −87 °C.

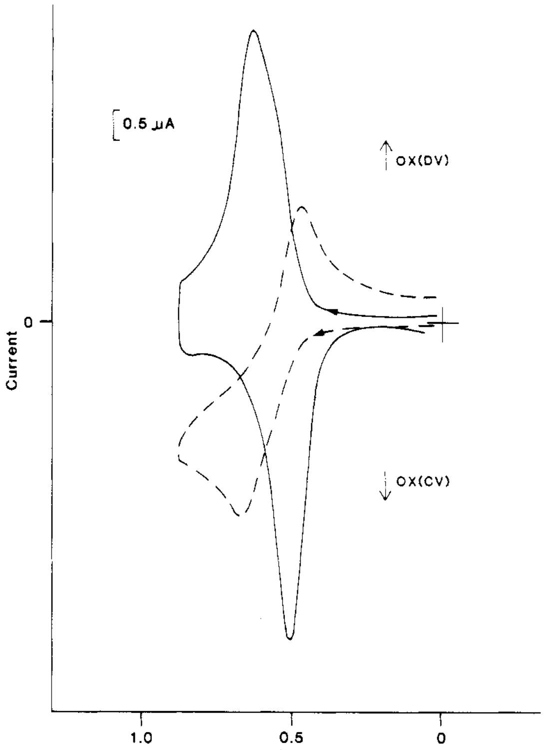

Figure 3. CV and DV curves for *E*/*Z* (0.5 mM) at −23 °C (v = 400 mV/s).

Similarly resolved oxidation peaks were obtained at −87 °C by using conventional differential pulse voltammetry with a pulse amplitude of 25 mV, but reproducibility was poor, apparently due to electrode fouling during the relatively long times required for this experiment. The DV technique is therefore preferred.

If the system *E*/*Z* is examined at −23 °C, the data shown in Figure 3 are obtained. The CV curve exhibits the characteristics of a single quasi-reversible one-electron oxidation process instead of the two chemically reversible processes observed at −87 °C. However, the anodic DV peak, which occurs at a potential intermediate between those observed at −87 °C, shows some distortion and broadening, which suggests that the process is still complex and may involve a modified form of the two processes seen at −87 °C. At this temperature the system exhibits apparent overall chemical reversibility as evidenced by DV (and CV) $i_p^{red.}/i_p^{ox.}$ values of 1.0 for $v > 100$ mV/s.

Insight into the complexities of this system is provided by examination of the partially isomerized mixture (*Z* + *E*) which is predominately *Z* as shown in Figure 4. Again, two reversible couples are clearly seen in the DV scans at −87 °C. Here the less positive couple ($E_{1/2}$ = 0.51 V) must be assigned to the oxidation of the predominate species *Z* while the more positive couple ($E_{1/2}$ = 0.66 V) is attributable to oxidation of *E*. At −63 °C this isomer mixture gives a similar pattern, with both couples resolved. The cathodic DV peak near 0.6 V associated with the reaction $E^+ + e \rightarrow E$ is, however, less evident at −63 °C and at lower scan rates. This is shown in Figure 5 which is a DV curve at v = 200 mV/s on an expanded potential scale.

Partially isomerized mixtures (*Z* + *E*) when examined at −23 and 22 °C give the patterns shown in Figures 3 and 1, respectively.

Finally this mixture, when left in contact with Al_2O_3 in 0.05 M $TBAPF_6$ overnight and then cooled to −87 °C, gives the CV and DV pattern of Figure 2, indicating that an equilibrium *E*/*Z* mixture which is predominately *E* is

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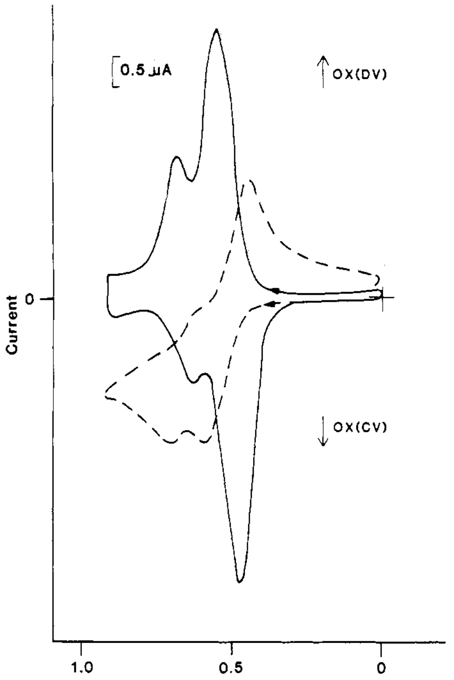

Figure 4. CV and DV curves for $Z + E$ (0.8 mM) at −87 °C (v = 400 mV/s).

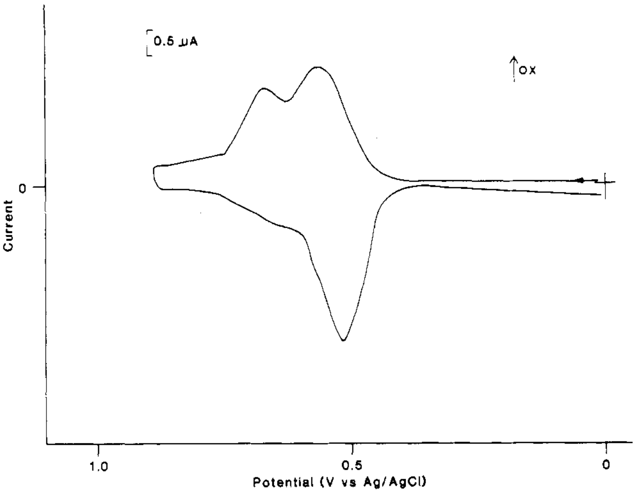

Figure 5. DV curves for $Z + E$ (1.1 mM) at −63 °C (v = 200 mV/s).

produced under these conditions. This is consistent with earlier synthetic studies.[10]

All of the above electrochemical results are consistent with Scheme I. The possibility of isomerization of the 18e species E and Z is not included as this reaction has been demonstrated to be slow even at room temperature in the absence of catalysts.[9]

Scheme I

$$Z \rightleftharpoons Z^+ + \mathrm{e} \quad E_{1/2}{}^{Z} \simeq 0.51 \text{ V vs Ag/AgCl at } -87\ {}^\circ\mathrm{C} \tag{4}$$

$$E \rightleftharpoons E^+ + \mathrm{e} \quad E_{1/2}{}^{E} \simeq 0.65 \text{ V vs Ag/AgCl at } -87\ {}^\circ\mathrm{C} \tag{5}$$

$$E^+ \rightarrow Z^+ \tag{6}$$

$$E^+ + Z \rightleftharpoons Z^+ + E \quad K_{\mathrm{eq}} = \exp\left[\frac{F(E_{1/2}{}^{E} - E_{1/2}{}^{Z})}{RT}\right] \tag{7}$$

Table I. Potential Data in CH_2Cl_2 (0.05 M $TBAPF_6$) from Deconvolution Voltammetric Curves at ν = 400 mV/s

system	T, °C	$E_p{}^{\mathrm{ox.}}$,[a] V	$E_p{}^{\mathrm{red.}}$,[a] V	$E_{1/2}$,[a] V
E/Z	−87	0.68[e]	0.62	0.65
		0.55	0.47[e]	0.51
	−23	0.65	0.50	0.57
	22	0.58	0.52	0.55
$Z + E$	−87	0.55[e]	0.47[e]	0.51
		0.68	0.64	0.66
	−63	0.56[e]	0.50[e]	0.53
		0.68	*b*	0.66[c]
	−23	0.61	0.51	0.56
	22	0.59	0.53	0.56
Z	−23	...	...	0.56[d]

[a] V vs Ag/AgCl; $E_{1/2}$ for oxidation of ferrocene = 0.42 V in 0.05 M $TBAPF_6$ at −87 °C. [b] Cathodic peak not sufficiently resolved for measurement at 400 mV/s. [c] From DV data at ν = 800 mV/s. [d] From CV data at ν = 200 mV/s. [e] Principal DV peak in cases where two reversible systems are resolved.

Additional confirmation of this scheme is provided by an examination of DV peak current ratios ($i_p{}^{\mathrm{red.}}/i_p{}^{\mathrm{ox.}}$) as a function of scan rate. While incomplete resolution precludes accurate measurement of the smaller peaks, the larger peaks can be measured on each voltammogram. At −87 °C in the equilibrium mixture (E/Z) this $i_p{}^{\mathrm{red.}}/i_p{}^{\mathrm{ox.}}$ ratio generally increases from a value less than 1 as v is decreased. Such behavior is expected if the principal anodic peak is due to the reaction $E \rightarrow E^+ + \mathrm{e}$ while the principal cathodic peak is due to $Z^+ + \mathrm{e} \rightarrow Z$, with the isomerization reaction $E^+ \rightarrow Z^+$ occurring on a time scale comparable with that of the experiment. Similarly, in mixtures ($Z + E$) that are predominantly Z the peak current ratio of the principal peaks (reduction/oxidation) deviates from near 1 to a higher value as v is decreased, reflecting more conversion of E^+ to Z^+ being observable at low scan rates. At −63 °C these $i_p{}^{\mathrm{red.}}/i_p{}^{\mathrm{ox.}}$ values for $E + Z$ followed the same trend that was observed at −87 °C but with higher values at all scan rates, consistent with more rapid conversion at the higher temperature. The second-order reaction predicted to occur via eq 7 is preceived to be important and to modify the system from that expected from purely first order isomerization reactions.

Thus, while it is not possible due to the complexity of the system to calculate rate constants from the DV data, several observations are clear: (1) At −87 and −63 °C separate reversible redox couples can be observed for the two isomers. (2) Even at −87 °C the conversion of E^+ to Z^+ is rapid on the time scale of conventional CV experiments. (3) At −23 °C the chemical reactions associated with eq 6 and 7 are sufficiently rapid to cause all isomer mixtures to exhibit the characteristics of a single chemically reversible system near the $E°$ value of the more easily oxidized isomer. (4) At room temperature the isomer mixtures also appear as a single system but with a decomposition reaction of the 17e product having a $t_{1/2}$ value of 0.4 s.

The isomer pairs examined thus represent an interesting case in which direct observation of both redox couples is possible at low (below ca. −63 °C) temperature while at higher (above ca. −23 °C) temperature electrochemical response indistinguishable from that of a single reversible one-electron system is observed. While the $E_{1/2}$ values measured at low temperatures are slightly influenced by coupled homogeneous reactions 6 and 7, the $\Delta E_{1/2}$ value still should provide a basis for the estimation of the equilibrium constant of reaction 7 and for calculation of the equilibrium ratio $[Z^+]/[E^+]$. From Table I, the $E_{1/2}{}^{E} - E_{1/2}{}^{Z}$ value is seen to be 0.14 ± 0.01 V in the range −63 to −87 °C. If −78 °C is chosen as the reference temperature, a value of K_{eq} of 4 × 10^3 for reaction 7 is calculated. This, combined with the equilibrium ratio ($[E]/[Z]$) of 4.7 at −78 °C from NMR data, gives $[Z^+]/[E^+] = 9 \times 10^2$. Thus, while in the neutral molecule the *E* isomer is slightly (2.5 kJ) favored, in the oxidized species the *Z* isomer is favored by 11 kJ. This distribution of isomers in the 17e species is consistent with the observed exclusive product in oxidatively induced CO insertion reactions of the acyl product derived from the *Z* isomer and may have implications for other synthetic chemistry in these compounds.

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Transition-Metal-Substituted Diphosphenes. 16.[1] [1 + 4] Cycloaddition of a Diphosphene to α,β-Unsaturated Carbonyl Compounds: Synthesis of Dihydro-1,2-λ⁵-oxaphospholes with Exocyclic P=P Bonds and X-ray Structure Analysis of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P[OCH=CHCH_2]}(=PAr)$ $(Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2)$

Lothar Weber,*,† Matthias Frebel,‡ and Roland Boese‡

Fakultät für Chemie der Universität Bielefeld, D-4800 Bielefeld 1, Germany, and Anorganisch-Chemisches Institut der Universität Essen, D-4300 Essen 1, Germany

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The reaction of $[(\eta^5\text{-}C_5Me_5)(CO)_2FeP{=}PAr]$ ($Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) (**1a**) with acrolein (**2a**), methacrolein (**2b**), and buten-3-one-2 (**2c**) in benzene at 20 °C afforded the transition-metal-functionalized dihydro-1,2-λ⁵-oxaphospholes $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P[OC(R^1){=}C(R^2)CH_2]}({=}PAr)$ (**3**) (**a**, $R^1 = R^2 = H$; **b**, $R^1 = H$, $R^2 = CH_3$; **c**; $R^1 = CH_3$, $R^2 = H$) with exocyclic P=P double bonds. The treatment of **1a** with crotonaldehyde (**2d**) at ca. 50 °C during 10 days yielded only an equilibrium mixture of the expected cycloadduct **3d** and the starting materials. A similar product, **3e**, was obtained from the corresponding ruthenium diphosphenyl complex **1b**. The novel heterocycles were characterized by elemental analyses and spectroscopic methods (IR, ^1H, ^{13}C, and ^{31}P NMR, and mass spectroscopy). The molecular structure of $(\eta^5\text{-}C_5Me_5)(CO)_2Fe\overline{P(OCH{=}CHCH_2)}{=}PAr$ was elucidated by a complete single-crystal diffraction study [$P2_1/n$ space group; $Z = 4$; a = 18.508 (4), b = 9.238 (3), c = 20.577 (5) Å; β = 99.71 (2)°].

Introduction

Low coordinated phosphorus compounds as phosphaalkenes $R^1P{=}CR^2R^3$, iminophosphanes $R^1P{=}NR^2$, and diphosphenes $R^1P{=}PR^2$ are potential candidates for ambident reactivity because they exhibit two high-lying molecular orbitals (π and n(P)) of similar energy.[2,3] Depending on the substitution pattern iminophosphanes tend to react in a carbene-like fashion documented in the [2 + 1] self-dimerization[4]

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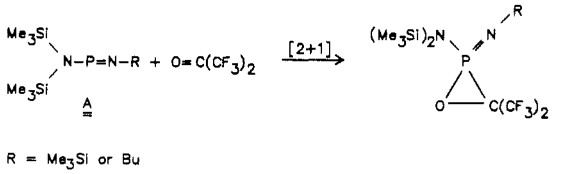
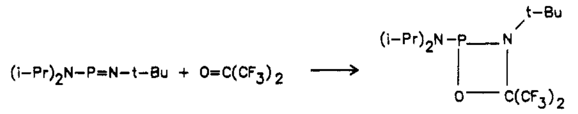
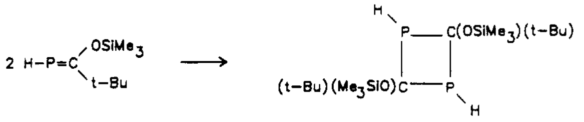


R = Me₃Si or Bu

or in an olefinic manner as shown in the [2 + 2] cyclodimerization with hexafluoroacetone[5a]



or its [2 + 2] self-dimerization.[5b] The [2 + 2] cycloaddition is well-documented for kinetically stabilized phosphaalkenes.[6]



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† Fakultät Für Chemie Universität Bielefeld.

‡ Anorganisch-Chemisches Institut der Universität Essen.

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