Oxidatively Induced Reductive Elimination from $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ and $Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)_2$

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In acetonitrile, the 16-electron species $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (1) and Ru(CHCHPh)- $(C_2Ph)(CO)(P^tBu_2Me)_2$ (2) exist as the corresponding 18-electron acetonitrile adducts. A single-crystal X-ray structure determination showed 1 to be square pyramidal with apical CO and the two acetylide ligands to be trans to each other. Crystal data (-90 °C): a =9.765(6) Å, b = 15.786(10) Å, c = 11.239(6) Å, $\beta = 99.87(3)^{\circ}$ with Z = 2 in space group P_{2_1} . The complexes undergo overall two-electron oxidation at 0.28 and 0.10 V vs Cp_2Fe/Cp_2Fe^+ , respectively. In dichloromethane 1 and 2 underwent 2-electron oxidations at 0.20 and 0.15 V. The lower oxidation potential of **2** compared to **1** is interpreted as an effect of the more electron-donating vinyl ligand. The electrochemical and chemical oxidations result in the intramolecular elimination of $[PhC_2]_2$ from 1 and $PhC_2CHCHPh$ from 2. In acetonitrile, $[Ru(CO)(NCMe)_3(P^tBu_2Me)_2](BF_4)_2$ (3(BF₄)₂) is formed as the main Ru-containing product. The main organometallic product in dichloromethane appears to exist as a $\text{Ru}(\text{CO})(L)_2^{n+}$ (*n* = 1, 2) fragment, possibly stabilized by interaction with solvent and/or counterion BF_4^- . A mechanistic and kinetic investigation of the elimination reactions by derivative cyclic voltammetry (DCV) showed the reductive eliminations from 1 and 2 to be first-order in 1^+ and 2^+ . The DVC analysis provided kinetic parameters for the reaction of 1^+ in acetonitrile and dichloromethane and for the reaction of 2^+ in MeCN. Oxidation of 1 in acetonitrile gave $k(0 \ ^{\circ}C) = 0.74 \ s^{-1}$, $\Delta H^{\ddagger} = 74.1(1.7) \ kJ/mol$, and $\Delta S^{\ddagger} = 5.9(5.4) \ J/(K \ mol)$ for the elimination from 1⁺, whereas the analysis in dichloromethane gave $k(0 \text{ °C}) = 0.93 \text{ s}^{-1}$, ΔH^{\pm} = 76.1(3.3) kJ/mol, and $\Delta S^{*} = 8.1(11.7) J/(K \text{ mol})$. For **2** in acetonitrile, $k(0 \text{ °C}) = 0.89 \text{ s}^{-1}$, $\Delta H^{\ddagger} = 61.9(5.4) \text{ kJ/mol}$, and $\Delta S^{\ddagger} = -6.4(20.1) \text{ J/(K mol)}$.

Introduction

Reductive elimination is a fundamental reaction frequently encountered in the product-forming step of catalytic and stoichiometric reactions in organic synthesis.¹ Stable organometallic complexes can be induced to undergo facile reductive elimination when subjected to oxidation. This is usually rationalized by the simple argument that an increase in the oxidation state increases the actual charge on the metal and hence makes reductive elimination more favorable.1a However, recent results have demonstrated that one-electron oxidations also have pronounced effects on M-H bond strengths. Thermochemical cycles have been used to probe the effect of one-electron oxidations on M-H bond strengths of $Tp'M(CO)_3H$ (Tp' = tris(pyrazolyl)borate; $M = Cr, W, Mo)^{2a}$ and various $CpCr(CO)_2LH$ complexes $(L = CO, PEt_3, PPh_3, P(OMe)_3)$ ^{2b} This revealed that oxidation led to a weakening of the W-H and Mo-H bonds by a relatively constant 108–113 kJ/mol toward

Scheme 1

$$Cp_{2}Ti \swarrow^{R}_{R'} \xrightarrow{-e^{-}}_{R'} \overset{R}{\longrightarrow} \overset{R}{\longrightarrow} \overset{R}{R'} + "Cp_{2}Ti^{+"}$$
1: R = 'Bu, R' = H
2: R = Me, R' = Me
3: R = 'Pr, R' = Me

$$Cp_{2}MPh_{2} \xrightarrow{-e^{-}}_{Ph \longrightarrow Ph} + PhH + "Cp_{2}M^{+"}_{M}$$

$$M = Ti, Zr$$

deprotonation and 25-33 kJ/mol toward homolysis. Another example demonstrating the bond-weakening effect of a one-electron oxidation is provided by Burk et al.^{3a} They found that reductive elimination occurred from the electron-poor, d⁰, 16-electron complexes shown in Scheme 1. The oxidations have been proposed to occur by removal of an electron from one M-C bond, thus weakening the bond.

Organometallic reactions such as ligand substitution, CO insertion, oxidative addition, and reductive elimination have traditionally been described in terms of 16-/ 18-electron interconversions. One-electron oxidations have been used to generate 17- and 19-electron species from 18-electron precursors. Accumulated evidence has established that much of the behavior of odd-electron complexes may be described in terms of 17/19 inter-

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conversions.⁴⁻⁷ Let us consider a reductive-elimination reaction from a 17-electron system. If the reductive elimination were to proceed directly, a highly unsaturated 15-electron product would result. Prior ligand coordination to a 19-electron intermediate avoids the formation of such a highly unsaturated product. Assuming that product stability is reflected in the energy of the transition state for the reductive elimination, 17-/19-electron interconversions certainly deserve to be considered for this reaction type. Kochi and co-workers⁸ have suggested that initial solvent ligation takes place in the elimination of biaryls from 16-electron Ar₂NiL₂ complexes, initiated by 1-electron oxidation to generate the reactive 15-electron cation radicals (Scheme 2). In this case, the formation of a 13-electron product is averted by prior ligand coordination.

Scheme 2

 $Ar_2Ni(PEt_3)_2 \xrightarrow{-e^-} Ar_2Ni(PEt_3)_2^+$ $Ar_2Ni(PEt_3)_2^+ \xrightarrow{fast} Ar_2Ni(PEt_3)_2(S)^+$ $Ar_2Ni(PEt_3)_2(S)^+ \xrightarrow{slow} Ar - Ar$

We report here the results of a study of the behavior of the 16-electron complexes $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (1) and $Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)_2$ (2) upon

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chemical and electrochemical oxidation. The use of the coordinating solvent acetonitrile and the virtually noncoordinating solvent dichloromethane in the oxidations opens up the possibility for probing the influence of the unsaturation of the metal center on the oxidatively induced reductive-elimination reaction. In addition, the possibility for the formation of two isomers of PhC₂-CHCHPh from 2 can yield valuable information about the mechanism of the the elimination reaction.

The reactions of both the bis(acetylide) 1 and the vinyl acetylide 2 are of potential relevance to the coupling of acetylenes to diynes and enynes. Traditionally this has been done in copper-mediated reactions,⁹ since copper readily forms both acetylene π -complexes and acetylides. Recently rhodium or palladium reagents have been used.¹⁰

Results

Synthesis, Characterization, and X-ray Structure of $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (1). The bis-(acetylide) compound $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2(1)$ can be synthesized in one pot from $RuHCl(CO)(P^tBu_2Me)_2$, equimolar amounts of LiC_2Ph , and 4-5 equiv of PhC_2H in hexane by the sequence of reactions shown in Scheme 3. Each step of the reaction has been individually demonstrated.11

Scheme 3

 $RuHCl(CO)(P^tBu_2Me)_2 \xrightarrow{PhC_2H}$

Ru(CHCHPh)Cl(CO)(P^tBu₂Me)₂

 $Ru(CHCHPh)Cl(CO)(P^tBu_2Me)_2 \xrightarrow{LiC_2Ph}$ $Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)_2$

$$\begin{array}{l} \operatorname{Ru}(\operatorname{CHCHPh})(\operatorname{C_2Ph})(\operatorname{CO})(\operatorname{P^tBu_2Me})_2 \xrightarrow{\operatorname{PhC_2H}} \\ \operatorname{Ru}(\operatorname{C_2Ph})_2(\operatorname{CO})(\operatorname{P^tBu_2Me})_2 + \operatorname{PhHC}\operatorname{CH_2} \end{array}$$

We reported earlier that ¹H, ¹³C, and ³¹P NMR data are consistent with C_{2v} symmetry for this molecule (Ia, where the value of θ is of course not established by such data) but could not rule out structure Ib, if the latter were still fluxional on the ${}^{13}C$ NMR time scale at -80°C.¹¹ We have now been able to grow crystals of 1, and a single-crystal X-ray structure determination (Figure 1, Table 1) shows Ia to be the correct representation, with $\theta = 169.0(15)^{\circ}$. While poor crystal quality left the

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Figure 1. Ball-and-stick drawing of the non-hydrogen atoms of $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Ru(C₂Ph)₂(CO)(P^tBu₂Me)₂ (1)

Ru(1) - C(4)	2.16(3)	Ru(1) - C(20)	2.05(8)
Ru(1) - C(12)	2.08(4)	O(21) - C(20)	1.22(7)
Ru(1) - P(2)	2.399(14)	C(4) - C(5)	1.18(5)
Ru(1) - P(3)	2.399(15)	C(12) - C(13)	1.21(6)
P(2) - Ru(1) - P(3)	176.3(10)	C(4) - Ru(1) - C(20)	85.0(21)
P(2) - Ru(1) - C(4)	85.5(9)	C(12) - Ru(1) - C(20)	90.4
P(2)-Ru(1)-C(12)	84.0(10)	Ru(1) - C(4) - C(5)	160.0(3)
P(2)-Ru(1)-C(20)	83.4(17)	C(4) - C(5) - C(6)	172.0(5)
P(3) - Ru(1) - C(4)	93.5(9)	Ru(1) - C(12) - C(13)	163.0(4)
P(3) - Ru(1) - C(12)	97.2(10)	C(12) - C(13) - C(14)	168.0(5)
P(3)-Ru(1)-C(20)	100.1(17)	Ru(1) - C(20) - O(21)	143.0(5)
C(4) - Ru(1) - C(12)	169.0(15)		

structure determination too inaccurate to merit detailed comparative discussion of bond lengths (e.g., the CO is



poorly determined), the overall coordination polyhedron is unambiguously determined. An examination of packing diagrams showed no evidence for significant intermolecular contacts involving the open coordination site (i.e., trans to CO).

The CO stretching frequency of 1, 1933 cm⁻¹, is higher than that observed for any RuHX(CO)(P^tBu₂Me)₂ species, including $X = C_2Ph$.¹¹ Since the donor power of H is less than that of C₂Ph, this led us to suggest that 1 did not have structure **Ib** (which is that preferred for all RuHX(CO)(P^tBu₂Me)₂ species except $X = SiR_3$), but rather structure **Ia**.

Synthesis, Characterization, and Structure of Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂Me)₂ (2). The execution of only the first two reactions (equimolar amounts of RuHCl(CO)(P^tBu₂Me)₂, LiC₂Ph, and PhC₂H in hexane) in Scheme 3 yields Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂-Me)₂ (2). The presence of the vinyl ligand is easily recognized by the characteristic resonances of the vinyl protons in the ¹H NMR spectrum (δ 8.62 (d) and 6.72 (d)). The magnitude of the ³J_{H-H} vinyl coupling constant (15 Hz) indicates their mutual *trans* stereochemistry.

We have established above that $Ru(C_2Ph)_2(CO)(P^tBu_2-Me)_2$ (1) conforms closely to square-pyramidal geometry. Similarly, it has been demonstrated that Os(CHCHPh)-Cl(CO)(P^iPr_3)_2 is square pyramidal, but with a basal CO and apical vinyl group.¹² On the basis of this, we assume that 2 is also square pyramidal with a basal



CO and apical vinyl group (II). This is supported by the low value of $\nu_{\rm CO}$ (1910 cm⁻¹). It indicates a greater degree of back-bonding than what may be expected for an apical CO *trans* to an empty site (compare with $\nu_{\rm CO}$ = 1933 cm⁻¹ for 1).

Coordination of Acetonitrile to 1 and 2. Both pyridine and nitriles (acetonitrile and acrylonitrile) are found to bind reversibly to $RuHX(CO)P_2$ species.¹³ When 4 equiv of acetonitrile was added to a red-orange solution of $RuH(C_2Ph)(CO)(P^tBu_2Me)_2$ in benzene- d_6 , a yellow solution was obtained.^{14a} The fading of color is consistent with a more "saturated" complex being formed from the 16-electron complex. The ³¹P NMR spectrum showed that the resonance for the phosphine changed from 53.2 to 56.5 ppm upon acetonitrile addition. At the same time v_{CO} changed from 1906 to 1896 cm⁻¹ and $\nu_{\rm CC}$ from 2072 to 2083 cm⁻¹. The increased back-bonding into the CO ligand verifies that acetonitrile indeed coordinates to the metal center. The Ru complexes 1 and 2 were suspected to show the same kind of behavior. Since we planned to use acetonitrile as the solvent in our investigation of the complexes, we were interested in finding out if the 16-electron nature of these complexes persisted when they were dissolved in acetonitrile.

The dark red Ru-hydrocarbyl compounds 1 and 2 are only moderately soluble in neat acetonitrile. The bis-(acetylide) 1 gave a yellow solution from which a pale yellow solid precipitated spontaneously. Complex 2 gave a red-orange solution from which red crystals were obtained. The solids from each solution were collected and dried in vacuo for 2-3 min. The dry compounds were dissolved in benzene- d_6 and analyzed by ¹H NMR spectroscopy. The spectra showed resonances for coordinated acetonitrile at δ 0.62 and 0.59 for 1 and 2, respectively. These resonances moved downfield to δ 0.69 (1) and 0.71 (2) upon addition of 10 μ L of acetonitrile- d_3 (free acetonitrile occurs at δ 0.73 when dissolved in benzene- d_6). The resonances at δ 0.69 and 0.71 are apparently average values for coordinated and uncoordinated acetonitrile. Thus, the experiments described above illustrate that acetonitrile indeed coordinates to the Ru centers and that fast exchange occurs between coordinated and uncoordinated acetonitrile.

Removal of the volatiles from acetonitrile solutions of 1 and 2 by pumping *in vacuo* for 12 h regenerated the 16-electron complexes free of coordinated acetonitrile (confirmed by ³¹P NMR and IR spectroscopy in benzene- d_6).

Addition of only 1 equiv of acetonitrile to a solution of 1 in benzene- d_6 gave immediate color change of the solution together with changes in the IR and ³¹P NMR

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 Table 2. Acetonitrile Coordination to 1 and 2

_	neat benzene-d ₆			benzene- d_6 + acetonitrile- d_3^a		
compd	color	³¹ P NMR (δ , ppm)	IR $\nu_{\rm CO}, \nu_{\rm CC} ({\rm cm}^{-1})$	color	³¹ P NMR (δ , ppm)	IR $\nu_{\rm CO}$, $\nu_{\rm CC}$ (cm ⁻¹)
1	dark red	47.7	1933, 2074	yellow	45.3	1940, 2081
2	dark red	40.9	1910, 2074	bright red	$40.9, 45.0^{b}$	1910, ^c 2074

^a The data are for addition of 1 equiv of acetonitrile to 1 and 20-30 equiv to 2. ^b Only a small amount (\sim 5%) of this peak was present. ^c A small shoulder (\sim 5%) was detected at higher frequencies.



spectra. For complex 2, however, 20-30 equiv of acetonitrile was needed to obtain detectable changes. The relevant spectroscopic data are summarized in Table 2.

Evidently there appears to be a certain degree of acetonitrile binding to the Ru complexes in question. The bonding is, however, more favorable to 1. The vinyl ligand of complex 2 is more electron donating than an acetylide ligand. Thus, 2 might be expected to be less electron deficient than 1 and consequently less susceptible to acetonitrile coordination. Working against this in 1 is the strongly *trans*-labilizing ligand CO *trans* to the empty site. Note, however, that we cannot rule out a structural change of 1 (Scheme 4) upon acetonitrile coordination. As a consequence, coordination of aceto-nitrile *trans* to CO would be avoided. This could also explain why $v_{\rm CO}$ increases from 1933 to 1940 cm⁻¹ instead of the decrease usually anticipated from the coordination of a donor ligand.

On the basis of these results, we conclude that 1 and 2 in acetonitrile exist as the corresponding 18-electron acetonitrile adducts. It has recently been reported that $RuHCl(CO)(P^iPr_3)_2$ binds acetonitrile.^{14b}

Thermal Stability of 1 and 2. Bergman and his group have previously investigated the thermal decomposition of $CpCo(PPh_3)RR'$.¹⁵ Facile reductive-elimination reactions resulted for alkyl-acyl and alkyl-vinyl complexes, whereas alkyl-alkyl complexes yielded mostly products from pathways other than reductive elimination. The elimination reactions occurred after initial phosphine dissociation from the 18-electron starting materials. These results were attributed to the ability of the alkyl-acyl and alkyl-vinyl systems to donate an additional electron pair to the metal in the transition state and make it a 16-electron species.

In our previous work with Cp*Rh(PPh₃)Me₂¹⁶ we found that the ease of ethane elimination from Cp*Rh-(PPh₃)Me₂^{•+} strongly contrasted with the extremely slow thermal decomposition of the neutral complex to yield only unknown products. The rate enhancement toward



Figure 2. Cyclic voltammogram for the oxidation of 1 in acetonitrile (0.1 M Bu₄NPF₆) at a Pt-disk microelectrode (d = 0.6 mm) at 0 °C and the voltage sweep rate v = 1.0 V/s.

reductive elimination due to one-electron oxidation was estimated to be at least a factor of 3×10^9 .

This motivated us to study the thermal behavior of 1 and 2 in order to be able to make a comparison of the thermal and oxidative behavior of these 16-electron species. Heating of sealed NMR tubes containing solutions of 1 and 2 in benzene- d_6 revealed that the complexes were stable at 62 $^{\circ}C$ for 24 h (by ¹H NMR). When the heating was continued at 74 °C for another 24 h, traces of free phosphine appeared in the ³¹P NMR spectra of the complexes. Prolonged heating at 84 °C yielded more phosphine. No other complexes were detected by ¹H NMR or ³¹P NMR spectroscopy. Even though the complexes are demonstrated to decompose slowly upon heating, there is no evidence for reductive elimination (i.e., there is no ¹H NMR evidence for formation of $[PhC_2]_2$ (from 1) and $PhC_2CHCHPh$ (from 2)). Note, however, that if thermal reductive elimination is to occur from 1, a structural change to yield a cis disposition of the organic moieties has to occur before the elimination can take place.

Cyclic Voltammetry Investigation of 1 and 2. Cyclic voltammetry (CV) was used for the initial investigation of the electrooxidation of 1 and 2. Two solvents, acetonitrile and dichloromethane, were chosen because of their different coordinating abilities. This will permit evaluation of the importance of the degree of unsaturation at Ru on the oxidatively induced elimination.

(a) First Oxidation Step. Figure 2 shows a cyclic voltammogram for the oxidation of 1 in acetonitrile (0.1 M Bu₄NPF₆, 0 °C, 0.6 mm diameter Pt-disk microelectrode, sweep width 1 V, voltage sweep rate v = 1.0 V/s). Peak a corresponds to the oxidation of 1, whereas peak b represents the reduction of 1⁺⁺ back to 1. The forward and reverse peaks are not of the same intensity. This indicates that a follow-up reaction partially consumes 1⁺⁺. The reversible oxidation potential of 1, taken to

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Figure 3. Cyclic voltammogram for the oxidation of **2** in dichloromethane (0.2 M Bu₄NPF₆) at a Pt-disk microelectrode (d = 0.6 mm) at 0 °C and the voltage sweep rate v = 1.0 V/s.

be the midpoint between the anodic and cathodic peaks, is 0.28 V vs the ferrocene/ferrocenium couple (Fc). Use of dichloromethane as solvent for the CV investigation of 1 gave a CV trace almost identical with the one already described for the investigation in acetonitrile, with a reversible oxidation potential of 0.20 V vs Fc. Admittedly, the difference between the oxidation potentials in the two solvents is not very large and it could be an effect of the great difference in polarity between the two solvents. Nevertheless, the opposite ordering of the oxidation potentials is expected, since an additional donor ligand is present when 1 is dissolved in acetonitrile. We have already speculated that 1 may undergo a structural change when it is dissolved in acetonitrile. The easier oxidation in dichloromethane can therefore be taken as another indication of such an isomerization.

The electrochemical oxidation of 2 in acetonitrile was also a partially reversible process at voltage sweep rate v = 1 V/s. In dichloromethane (0.2 M Bu₄NPF₆), however, the reaction was close to reversible. This is depicted in Figure 3. The reversible oxidation potentials were found to be 0.10 and 0.15 V vs Fc in acetonitrile and dichloromethane, respectively. Note that the oxidation of 2 is easier to accomplish than the oxidation of 1. This is probably because the vinyl ligand in 2 donates more electron density to the metal center than the acetylide ligand in 1. While the difference of 0.05 V between the oxidation potentials of 2 in the two solvents is small, the difference is in the expected direction, assuming that acetonitrile coordination increases the electron density of 2.

(b) Second Oxidation Step. We infer from the partial chemical reversibility of the oxidation of 1 and 2 that their cation radicals are rather stable (half-life of a few seconds). An increased sweep width (from 1 to 1.6 V) in the cyclic voltammetry experiment of 1 in acetonitrile showed (Figure 4) that the radical cation, 1^{++} , underwent oxidation to yield 1^{2+} (peak c). In addition to confirming that 1^{++} is indeed relatively stable, it also provides information about the electron density of the metal. The occurrence of a second oxidation was least surprising when acetonitrile was used as solvent, since we have shown that acetonitrile is coordinated to the metal. However, the dication was also generated in dichloromethane, and the irreversible



Figure 4. Cyclic voltammograms for the oxidation of 1 in acetonitrile (0.1 M Bu₄NPF₆) at a Pt-disk microelectrode (d = 0.6 mm) at 0 °C. Trace A (lower trace) shows the process at the voltage sweep rate v = 1.0 V/s, whereas trace B (upper trace) shows it at the voltage sweep rate v = 0.2 V/s.

peak potentials for oxidation of $1^{\cdot+}$ were found to be practically identical in the two solvents (1.12 and 1.10 V vs Fc in acetonitrile and dichloromethane, respectively). If we assume that acetonitrile indeed increases the electron count on Ru, something else must play this role when dichloromethane is used as solvent. The identity of such a species is unknown but could be weakly bound counterion BF_4^{-} ,^{17a} dichloromethane,^{17b-d} or traces of adventitious water.

The difference between the first and the second oxidations of 1 (i.e. peaks a and c), in both acetonitrile and dichloromethane, is 0.8-0.9 V. If the kinetic potential shifts of irreversible reactions¹⁸ are taken into account, the difference is probably even larger. In any case, the potential difference is in accord with previous results, where the oxidation potentials for the oxidation of 17-electron radicals to 16-electron cations were found to be 0.8-1.2 V more positive than those for the oxidation of the corresponding 18-electron anions to radicals.²

As already mentioned, Figure 4 depicts CV traces for the oxidation of 1 in acetonitrile with sweep widths of 1.6 V. Peak **a** corresponds to the partially reversible oxidation of 1 (as in Figure 2), whereas peak **c** is the irreversible oxidation of 1^{++} to 1^{2+} . As evidenced by the irreversibility of this second oxidation, the dication is unstable and reacts quickly. In the system described above, slower sweep rates will increase the extent of decay of 1^{++} on the experimental time scale. Consequently, the intensity of peak **c** relative to a should decrease with decreasing sweep rate. This is illustrated by the two traces in Figure 4. Trace A depicts the

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$$Ru = Ru(CO)(NCMe)(P^{t}Bu_{2}Me)_{2} \text{ in MeCN}$$

$$Ru = Ru(CO)(P^{t}Bu_{2}Me)_{2} \text{ in CH}_{2}Cl_{2}$$

$$C = C_{2}Ph \text{ for } 1$$

$$C = C_{2}Ph \text{ and CHCHPh for } 2$$

^{*a*} $AcFc^+ = acetylferrocenium.$

process at v = 1.0 V/s, whereas trace B is for v = 0.2 V/s. By comparison of the voltammograms, it is evident that the relative intensity of peak **c** is significantly diminished. In an attempt to establish the identity of the species undergoing reduction at peak **d**, the scan was reversed at 0.8 V, i.e. just before oxidation to the dication takes place. Peak **d** did not appear at any sweep rate (0.2-10.0 V/s), nor did it gain intensity when the dicationic complex [Ru(CO)(CNMe)₃(P^tBu₂Me)₂]-(PF₆)₂ (3(PF₆)₂; vide infra) was added to the solution. Thus, peak **d** arises not from the decomposition of 1^{•+} but from 1²⁺, and it is not due to the dicationic complex **3** (3 did not show electroactivity from -1.6 to +1.8 V vs Fc).

Increasing the sweep width from 1 to 2 V in the cyclic voltammetry investigation of **2** in acetonitrile also gave a second oxidation peak. The oxidation potential was determined to be 1.10 V vs Fc. In contrast to what was observed for $1^{\bullet+}$, the oxidation of $2^{\bullet+}$ was partially reversible. A broad, ill-defined wave at ca. 1 V vs Fc was seen when the sweep width was increased from 1 to 2 V in dichloromethane solvent.

(c) Summary of Cyclic Voltammetric Processes. On the basis of the discussion above, a schematic overview over all of the processes is shown in Scheme 5. The processes giving rise to peaks $\mathbf{a}-\mathbf{d}$ (Figure 4) are marked with the corresponding letters in parentheses. Steps involving acetonitrile do not, of course, occur in dichloromethane. The oxidation of "Ru⁺" is not observed as a separate peak because it (most likely after acetonitrile coordination)¹⁹ presumably undergoes oxidation at the potential where 1 (2) is oxidized. The chemical oxidation of 1 and 2 (vide infra) follows path A. The oxidizing agent used (acetylferrocenium tetrafluoroborate, or [AcFc]BF4, 0.248 V vs Fc) is not powerful enough to act as an effective oxidant toward $\mathbf{1}^+$ and $\mathbf{2}^+$ to produce $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$, respectively.

Constant-Current Coulometry of 1 and 2. Constant-current coulometry experiments, in which the substrate consumption was monitored by derivative cyclic voltammetry (DCV), were used to find the amount of charge (faraday/mol) needed for complete substrate consumption under electrochemical conditions. Constant-current coulometry experiments (acetonitrile, 0.05 M Me₄N(BF₄)) required the passage of 2.0 faraday/mol of charge for complete consumption of 1 and **2**. This is indicative of an overall two-electron process on this time scale (5–10 min). Analysis of the resulting solutions by ³¹P NMR spectroscopy showed formation of [Ru(CO)(NCMe)₃(P^tBu₂Me)₂](BF₄)₂ (**3**(BF₄)₂). The following paragraphs will show that **3** is also the main metal-containing product for the chemical two-electron oxidations of **1** and **2** in acetonitrile.

Chemical oxidations of 1 and 2 were found to consume 2 equiv of AcFc⁺ in acetonitrile and dichloromethane (vide infra). Constant-current coulometry experiments with dichloromethane (0.2 M Bu₄N(PF₆)) as solvent only consumed 1.5 and 1.3 faraday/mol for complete oxidation of 1 and 2, respectively. The source of the discrepancy between the coulometric experiments and the homogeneous experiments is believed to be that the reaction of the cation radicals 1^{•+} and 2^{•+} under the experimental conditions for the coulometric experiments generates products that are electroinactive.

Homogeneous Outer-Sphere Oxidation of 1 in Acetonitrile and in Dichloromethane. Oxidation of 1 in acetonitrile was first attempted with 2 equiv of (Cp₂- $Fe)(PF_6)$ (note that Cp_2Fe/Cp_2Fe^+ (Fc) is used as reference (0 V) in the CV experiments). This reaction turned out to be rather slow; full consumption of the oxidant occurred only after 4-5 h and yielded a mixture of several products (by ³¹P NMR). To increase the speed of the oxidation, the more potent oxidant acetylferrocenium tetrafluoroborate $(AcFc(BF_4))$ was employed. This gave immediate consumption of the oxidant and a cleaner reaction. The main phosphorus-containing product (42.4 ppm by ³¹P NMR spectroscopy) was 75-80% of the total yield of products. There were also four other weak signals. It was also established (by ¹H NMR) that the order of addition influenced the relative yield of main products and byproducts. Relatively slow addition of ruthenium complex (20 mg) in acetonitrile $(\sim 25 \text{ mL})$ to 2 equiv of AcFc(BF₄) (in 5 mL of acetonitrile) gave only the main product and traces of one byproduct (~95:5) by inspection of ³¹P NMR spectra.

Titration of an acetonitrile solution of $AcFc(BF_4)$ with the bis(acetylide) 1 confirmed that 2 equiv of oxidant was required to consume 1 equiv of 1.

After oxidation, a typical ¹H NMR spectrum showed a cluster of peaks in the area 7.3-7.8 ppm and two virtual triplets at δ 1.40 and 1.60 ppm (^tBu and Me) in addition to peaks for acetylferrocene. The resonances at 1.40 and 1.60 ppm arise from an organometallic product, which was identified as [Ru(CO)(NCMe)₃- $(P^{t}Bu_{2}Me)_{2}](BF_{4})_{2}$ (3(BF_{4})_{2}). The phosphine resonance for **3** is identical (42.4 ppm) with the resonance for the main product detected above with ³¹P NMR. The yield of 3 was found to be 75% (¹H NMR) when hexamethylbenzene was added as internal standard for product quantification. The independent synthesis and identification of this dication are described in the following section. Extraction (Et_2O) of the dried residue from oxidation, followed by ¹H NMR analysis of the ether extract, established that the peaks in the phenyl region originated from an ether-soluble product. Comparison to an authentic sample of $[PhC_2]_2$ (¹H and ¹³C NMR and mass spectrometry) proved that this diyne was formed in the reaction (72%). In addition, there was no

⁽¹⁹⁾ It has been previously shown that the oxidizing potential of a cation radical M^{*+} is lowered by ~ 1.3 V upon acetonitrile coordination: Skagestad, V.; Tilset, M. Organometallics **1991**, *10*, 2110.

evidence for formation of PhC_2H (detection limit 3%), a product expected if homolytic cleavage of the Ruacetylide bond were followed by cage escape and H atom abstraction.

The oxidation of 1 with $AcFc^+$ in dichloromethane solvent was also found to be a two-electron process. The best conditions for the oxidation were again addition of bis(acetylide) to $AcFc^+$, but less solvent (3-5 mL) was used, due to better solubility of the substrate in dichloromethane. Again $[PhC_2]_2$ was identified as the only organic product (47% yield).

The oxidation in dichloromethane resulted in a complex organometallic product mixture. A main product together with several byproducts were detected by ³¹P and ¹H NMR. In addition, it was evident from the IR spectrum that two main products were present. Two overlapping CO stretches were observed. One of them may arise from an NMR-silent (paramagnetic) compound. The yield of the NMR-detectable product and byproducts varied from experiment to experiment. Quantification of a typical experiment showed 53% yield of the main product. The spectroscopic data in dichloromethane (³¹P, ¹³C, and ¹H NMR and IR) indicate that the product is a cationic complex containing a CO ligand and two phosphine ligands per Ru center. The ¹H NMR spectrum showed a doublet for 'Bu and a doublet of doublets for the methyl. Thus, it has a very different coupling pattern compared to the product formed in acetonitrile. However, when the solvent was removed from a typical reaction mixture and the residue dissolved in acetonitrile- d_3 , ³¹P NMR spectroscopy showed the resulting mixture to consist mostly of complex 3. The ${}^{1}H{}^{31}P{}$ NMR spectrum of a dichloromethane solution consisting mostly of the main product from the oxidation in dichloromethane gave a broad singlet for ^tBu and a broad peak for the methyl group. The peak width of the ³¹P NMR signal was measured to be 6 Hz. This is broader than expected (2-3 Hz) but not extremely broad. The conclusion is that a fluoride ligand is not coordinated to Ru. This statement is supported by the ¹⁹F NMR spectrum of the product mixture, which showed no resonance for a F-ligand (in the range of +50to -450 ppm). The ¹⁹F NMR spectrum did not show the normal signal for the counterion BF_4^- but rather a very broad peak in the vicinity (i.e., within ~ 0.5 ppm) of the normal resonance for BF_4^- . Lowering of the temperature to -90 °C did not bring any change of the ¹⁹F NMR spectrum. We propose a weak coordination of the BF₄⁻ counterion to the product from the dichloromethane oxidation.^{17a} In addition, stabilization of the product by adventitious traces of water or dichloromethane cannot be ruled out.

Characterization of [Ru(CO)(NCMe)₃(**P**^{*}**Bu**₂**Me**)₂]-(**BF**₄)₂ (**3(BF**₄)₂). The dicationic acetonitrile adduct **3** was identified by ¹H, ¹³C, and ³¹P NMR and IR data.²⁰ The IR spectrum showed a ν_{CO} stretching frequency of 2010 cm⁻¹. Compared to the values of 1933 and 1910 cm⁻¹ for **1** and **2**, respectively, this indicates that the back-bonding to CO is greatly diminished in complex **3**, as expected for a dicationic complex. The ¹H NMR spectrum of **3**(BF₄)₂ in CD₃NO₂ showed one virtual triplet for P^tBu and one for PMe, indicating *trans* phosphine groups. The spectrum also revealed two resonances in a 1:2 ratio for coordinated acetonitrile. Therefore, the bis(acetonitrile) adduct **3** was assigned the structure **III**.



The sterically demanding phosphine groups in 1 and 2 interfere with the binding of potential ligands as acetonitrile, pyridine, and $H_{2.}^{13}$ In addition, the CO ligand is generally viewed as a ligand with a strong *trans* effect. Thus, the acetonitrile ligand *trans* to CO is expected to be rather labile. This was confirmed when $3(BF_{4})_2$ was dissolved in acetonitrile- d_3 . The acetonitrile resonance of only one of the acetonitrile ligands disappeared within $1/_2$ h due to exchange with CD₃CN. The remaining two MeCN ligands undergo no detectable exchange with neat CD₃CN over the course of 2 days at 25 °C.

Investigation of the Molecularity of the Reductive Elimination from 1. We sought to establish whether the C-C bond-forming reaction which produces the diyne was of intramolecular or intermolecular nature. An intermolecular reaction could be viable for several reasons. First, acetylide is known to frequently serve as a bridging ligand (IV).²² There is thus a



plausible way for an intermolecular mechanism to begin. The possibility of a intermolecular reaction is even more likely, considering that the acetylide ligands in 1 are mutually *trans*, a sterochemistry unsuitable for prompt unimolecular reductive elimination. However, it is not necessarily true that the oxidized species, 1^{*+} , has a *trans* geometry.

For this purpose, we employed $\operatorname{Ru}[C_2(p-\operatorname{tolyl})]_2(\operatorname{CO})(\operatorname{Pt-Bu}_2\operatorname{Me})_2$ as an alternative to an isotopically substituted derivative of 1. It was first established that oxidation $(\operatorname{AcFc}(\operatorname{BF}_4))$ of $\operatorname{Ru}[C_2(p-\operatorname{tolyl})]_2(\operatorname{CO})(\operatorname{PtBu}_2\operatorname{Me})_2$ in acetonitrile produced $[(p-\operatorname{tolyl})C_2]_2$, which shows an electronimpact mass spectrum parent ion at m/e 230. In the crossover experiment, a mixture of equimolar amounts of 1 and $\operatorname{Ru}[C_2(p-\operatorname{tolyl})]_2(\operatorname{CO})(\operatorname{PtBu}_2\operatorname{Me})_2$ was oxidized in acetonitrile. Mass spectral analysis of the ether-soluble material resulting from the oxidation showed m/e 230 for $[(p-\operatorname{tolyl})C_2]_2$ and m/e 202 for $[\operatorname{PhC}_2]_2$ but no signal above the base line at m/e 216 for the crossover diyne $(p-\operatorname{tolyl})C_2C_2\operatorname{Ph}$. The C-C bond formation, therefore,

⁽²⁰⁾ Several attempts to independent by synthesize $[Ru(CO)(NCMe)_3-(P^tBu_2Me)_2](BF_4)_2\ ({\bf 3}(BF_4)_2)$ were unsuccessful.

⁽²¹⁾ It was impossible to obtain an acceptable elemental analysis due to inseparable impurities formed in the oxidation reaction.

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S. F. T.; Green, M.; Mercer, R. J.; Nagle, K. R.; Orpen, A. G.; Rodrigues, A. J. Chem. Soc., Dalton Trans. 1991, 3171.

takes place intramolecularly (Scheme 6).

Scheme 6

$$\begin{aligned} \operatorname{Ru}(\operatorname{C_2Ph})_2(\operatorname{CO})(\operatorname{P^tBu_2Me})_2 + \\ \operatorname{Ru}[\operatorname{C_2}(p\text{-tolyl})]_2(\operatorname{CO})(\operatorname{P^tBu_2Me})_2 \xrightarrow{-2e^-} \\ \operatorname{PhC} \equiv \operatorname{CC} \equiv \operatorname{CPh} + [(p\text{-tolyl})\operatorname{C_2}]_2 \end{aligned}$$

The same series of experiments were repeated, but this time with dichloromethane as solvent. Again mass spectrometric analysis showed that the reaction was intramolecular.

Homogeneous Outer-Sphere Oxidation of 2 in Acetonitrile and in Dichloromethane. The oxidation of 2 in acetonitrile and dichloromethane showed great similarities with the oxidation of 1. The twoelectron oxidation $(AcFc(BF_4))$ of 2 in acetonitrile and dichloromethane also resulted in elimination of the organic moieties (Scheme 7). In acetonitrile, [Ru(CO)-



 $(NCMe)_3(P^tBu_2Me)_2](BF_4)_2$ (3 $(BF_4)_2$, 75%) was formed, whereas the mixture of metal-containing products in dichloromethane was the same as the product mixture from the oxidation of 1 in dichloromethane. The main product was found in 42% yield.

Ether extraction of the dried residues from the oxidations yielded the E and Z isomers (9:1) of the enyne PhC₂CHCHPh. The yield of enyne was 70% in acetonitrile and 46% in dichloromethane. Both solvents gave the same isomeric ratio (E/Z = 9/1). The identities of the enyne and the separate isomers were established by comparison with literature ¹H and ¹³C NMR data.²³ The (E)-enyne was also identified by comparison with a compound formed in an independent synthesis.²⁴

Investigation of the Formation of (E)- and (Z)-**PhCHCHC**₂**Ph.** It is already established that the reductive elimination of $[PhC_2]_2$ from $Ru(CCPh)_2(CO)$ - $(P^tBu_2Me)_2(1)$ is an intramolecular reaction. We wanted to confirm that (E)- and (Z)-PhC₂CHCHPh also were formed intramolecularly. An intermolecular reaction was expected to yield $[PhC_2]_2$ and $[PhCHCH]_2$ in addition to $PhC_2CHCHPh$. The organic components from the oxidation of 2 were analyzed by capillary gas chromatography (GC). Examination of the GC traces revealed that 2.5-3.0% of $[PhC_2]_2$ was formed in either solvent. At least some of this could originate from 1 as an impurity in our sample of 2. There was no evidence for formation of PhC₂H, the product expected if homolytic cleavage of the Ru-acetylide bond were followed by cage escape.



^{*a*} $AcFc^+ = acetylferrocenium.$

We have sought to establish whether the formation of enyne double-bond geometric isomers is inherent to the mechanism of the oxidatively induced reductive elimination reaction or whether it is a consequence of isomerization of free enyne product by a component of the reaction mixture subsequent to C-C bond formation.

To test for the possible isomerization of (E)-PhC₂-CHCHPh by unconsumed oxidant, AcFc(BF₄) and (E)-PhC₂CHCHPh were dissolved in dichloromethane- d_2 . Even after 24 h no isomerization of the enyne was observed. The same was found when (E)-enyne was added to a solution of products from the oxidation of Ru(CHCHPh)(C₂Ph)(CO)(PtBu₂Me)₂ (2) in dichloromethane. Thus, neither unconsumed oxidant nor the organometallic products from the oxidation in dichloromethane were found to effect isomerization (Scheme 8).²⁵

From the CV experiments it is known that the cation radical 2^{*+} has a half-life of several seconds. Hence, there is time for an isomerization of the vinyl ligand to occur, giving small amounts of 2^{*+} with *cis* disposition about the double bond of the vinyl ligand. From this isomerized cation radical, isomerized 2 could be obtained upon oxidation of unconsumed 2 by 2^{*+} . This was investigated by treatment of solutions of 2 (acetonitrile and dichloromethane) with 0.4 equiv of AcFc⁺. Analysis of the extracts from the dried residues of the reaction showed no change of the unconsumed 2. There were no new ¹H NMR resonances in the vinyl region and no changes in the ³¹P NMR spectra. Thus, the vinyl stereochemistry in 2 is unchanged under the reaction conditions.

Kinetics of the Reductive Elimination from 1^{•+} and 2^{•+}. When conventional CV is employed as a tool for the investigation of electrode processes or of the reactions of electrogenerated species, the double-layer charging current causes a distortion of the base line. This poses a problem for kinetic applications of CV, especially at high voltage sweep rates and/or low substrate concentration, where the charging current may be dominant. The use of derivative cyclic voltammetry¹⁸ (DCV) circumvents this problem.

DCV has been established as a powerful tool for the investigation of the mechanism and kinetics of organic and organometallic electrode reactions.²⁶ The parameter of interest for the discussion to follow is v_c , defined

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⁽²⁴⁾ Kern, R. J. Chem. Commun. 1968, 706.

⁽²⁵⁾ Since the ratios of isomers formed in the oxidation reactions were identical, we assume that what is valid in dichloromethane also is valid in acetonitrile. Hence, the experiments were not repeated in acetonitrile.

⁽²⁶⁾ For some recent examples of the use of DCV in organic and organometallic chemistry, see: (a) Parker, V. D.; Tilset, M. J. Am. Chem. Soc. 1986, 108, 6371. (b) Reitstøen, B.; Norrsell, F.; Parker, V. D. J. Am. Chem. Soc. 1989, 111, 8463. (c) Parker, V. D.; Reitstøen, B.; Tilset, M. J. Phys.-Org. Chem. 1989, 2, 580. (d) Reitstøen, B.; Parker, V. D. J. Am. Chem. Soc. 1990, 112, 4968. (e) Parker, V. D.; Chao, Y.; Reitstøen, B. J. Am. Chem. Soc. 1991, 113, 2336. (f) Reitstøen, B.; Parker, V. D. J. Am. Chem. Soc. 1991, 113, 6954. (g) Tilset, M. In Energetics of Organometallic Species; Simões, J. A. M., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; p 109.



Figure 5. Reaction-order plot of log $v_{0.6}$ vs log C based on DCV analysis of the oxidation of $1 (\Box)$ and $2 (\bullet)$ in acetonitrile (0.1 M Bu₄NPF₆) at a Pt-disk microelectrode (d = 0.6 mm) at 0 °C and the voltage sweep rate v = 1.0 V/s.

as the voltage sweep rate which for fixed experimental conditions causes the cathodic $(I_{p,c})$ to anodic $(I_{p,a})$ derivative peak current ratio $(\mathbf{R'}_{\mathbf{I}})$ to be equal to c. The value of the method is readily appreciated if one consider the case of c = 0.5. Here, the time lag between the detection of the oxidation peak and the reduction peak correlates with the half-life of the electrodegenerated intermediate. For different experimental conditions, v may be fine-tuned to determine $v_{0.5}$. The parameter $v_{0.5}$ provides valuable kinetic information, since it is directly proportional to the rate constant for the chemical reaction consuming the primary CV product.¹⁸ Provided that the separation between the scan reversal potential (E_{sw}) and the reversible electrode potential for the compound studied in a series of experiments is maintained at a constant value, DCV may be used in reaction-order analyses²⁸ to establish the rate law for the follow-up reaction.

DCV reaction-order analyses were carried out on the radical cation formed in the oxidation of bis(acetylide) 1 and the vinyl complex 2 in acetonitrile and dichloromethane. The substrate concentrations in each experimental series were varied in the range 1-4 mM. The reaction-order plot in Figure 5 depicts log $v_{0.6}$ vs $\log C$ for both substrates. The slopes of the correlation lines are close to zero (0.01 for 1 and 0.03 for 2); thus, the reactions of 1.+ and 2.+ in acetonitrile are first order in [1⁺⁺] and [2⁺⁺], respectively. This is consistent with our determinations from crossover experiments. A reaction-order analysis of 1 in dichloromethane showed that the reaction was also first order in 1^{++} in this solvent. As was already established, the oxidation of 2 in dichloromethane is close to reversible. It allowed the measurement of a single rate constant, assuming a firstorder reaction of 2.+, but made measurements of reaction order and temperature effects in dichloromethane impractical because voltage sweep rates under some conditions were too slow for accurate measurements to be attainable.

The rate of reaction of Cp*Ru(CO)(PPh₃)CH₃•+ has previously been demonstrated to be strongly solvent dependent.²⁷ The rate enhancement upon changing the



Figure 6. Observed rate constant vs the acetonitrile concentration (% v/v) for the chemical reaction of $2^{\bullet+}$ in acetonitrile/dichloromethane (0.1 M Bu₄NPF₆) mixtures.



Figure 7. Arrhenius type plot^{28} of $\ln(v_{0.6}/T)$ vs 1000/T for the reaction of 1^{++} (1.0 mM) in acetonitrile (0.1 M Bu₄NPF₆) at a Pt-disk microelectrode (d = 0.6 mm).

solvent from dichloromethane to acetonitrile was estimated to be at least a factor of 2000. The reaction-order analysis of **1** in acetonitrile and dichloromethane, however, showed that the $v_{0.6}$ values were almost identical in the two solvents. The occurrence of possible rate enhancement for the reaction of $2^{\bullet+}$ in acetonitrile was also checked. The result is depicted in Figure 6. Addition of acetonitrile certainly has an effect, but it can by no means be compared to what is observed for the decomposition of $Cp^*Ru(CO)(PPh_3)CH_3^{\bullet+}$.

Organometallic compounds of weakly coordinating anions, e.g., BF_4^- , PF_6^- , and AsF_6^- , have been the object of many studies in recent years.¹⁷ Hence, these counterions cannot always be considered to be "innocent". Close ion pairing has been reported to affect the kinetics of halide-induced disproportionation reactions of the 17electron cations $M(CO)_3(PCy_3)_2^{\bullet+}$ (M = Fe, Ru, Os) in dichloromethane.^{17e} The possible intervention of the counterion PF_6^- was investigated for complex 2. The electrolyte concentration was varied between 0.05 and 0.3 M in dichloromethane. This gave no significant change in the reaction rate (i.e., $v_{0.6}$) of $2^{\bullet+}$.

Variable-temperature measurements of $v_{0.6}$ for the processes in acetonitrile, yielded the Arrhenius type plots in Figures 7 (1) and 8 (2). The experiment was repeated for 1 in dichloromethane. This gave a curve almost identical with that for 1 in acetonitrile. Linear regression based on the data from three independent runs (for 1 and 2 in acetonitrile and for 1 in dichlo-

⁽²⁷⁾ Tilset, M.; Aase, T. In *Natural Gas Conversion*; Holmen, A., Jens, K.-J., Kolboe, S., Eds.; Elsevier: Amsterdam, 1991; p 197. (28) $\ln v_{0.6}/T$ is proportional to the rate constant.¹⁸



Figure 8. Arrhenius type plot of $\ln(v_{0.6}/T)$ vs 1000/T for the reaction of **2**^{•+} (1.0 mM) in acetonitrile (0.1 M Bu₄NPF₆) at a Pt-disk microelectrode (d = 0.6 mm).

Table 3. Kinetic Data for 1 and 2

compd	E _a (kJ/mol)	ΔH^{\ddagger} (kJ/mol)	ΔS^* (J/(K mol))	<i>k</i> (0 °C) (s ⁻¹)
1 ^a	78.5(3.3)	76.1(3.3)	8.1(11.7)	0.93
1^{b}	76.4(1.3)	74.1(1.7)	5.9(5.4)	0.74
2^{b}	62.1(4.5)	61.9(5.4)	-6.4(20.1)	0.89

 a In dichloromethane (0.2 M Bu_4N(PF_6)). b In acetonitrile (0.1 M Bu_4N(PF_6)).

romethane) yielded activation energies for the subsequent chemical reactions. These data are given in Table 2.

The information at hand from DCV, coulometry, and observed products is in agreement with an ECE mechanism in which the chemical reaction is a first-order elimination of $[PhC_2]_2$ and $PhC_2CHCHPh$ from 1^{•+} and 2^{•+}, respectively (path A in Scheme 5). The experimental $v_{0.6}$ values may be compared with theoretical data for this mechanism obtained by digital simulation for a first-order ECE mechanism with rate law (r) given as $r = -k[1^{•+}]$. The resulting rate constants and activation parameters are given in Table 3.

We have seen that samples of 1 and 2 in benzene- d_6 decompose very slowly at 74 °C to yield P^tBu₂Me as the only detectable product (5% after 24 h). By extrapolation to 74 °C, the rates of reaction of 1^{•+} and 2^{•+} are 326 and 63 s⁻¹, respectively. Thus, the rate enhancement due to the one-electron oxidations amounts to at least a factor of 3×10^8 !

Discussion of Electrolyte Effects on the Kinetics of the Reductive-Elimination Reactions of 1 and 2. We have concluded that 1 and 2 most likely exist as the corresponding 18-electron acetonitrile adducts when dissolved in acetonitrile. Hence, when the experiments are done in the two solvents acetonitrile and dichloromethane, different species are investigated (1(NCMe) and 2(NCMe) vs 1 and 2). It was therefore rather surprising to discover that the oxidation potentials, the rate constants for the subsequent chemical reactions, and the kinetic parameters were little affected by the solvent. The similarities can of course be coincidental, but traces of water, weak coordination of dichloromethane, or coordination of the counterion BF4⁻ could enhance the reactions in dichloromethane and at least in part conceal actual differences.

Variation of the electrolyte concentration in dichloromethane did not significantly influence the rate of reaction of 2^{*+} . This might imply no assistance of BF₄⁻ in the reductive elimination. However, the concentra-



tion of BF_4^- is immense (even at the lowest $[BF_4^-]$ studied here) compared to the concentration of substrate. Thus, there can already be saturation of BF_4^- coordination even at an electrolyte concentration of 0.05 M. Close ion pairing between $1^{+}/Ru(CO)(P^tBu_2Me)_2^{+}$ and BF_4^- can also occur. This would give reductive elimination from strongly ion-paired species in dichloromethane and thus prevent the formation of a formally 13-electron species, $Ru(CO)(P^tBu_2Me)_2^{+}$. The observed lack of dependence of the reaction rate on the concentration probably implies that the BF_4^- counterion does not actively assist the reductive-elimination reaction. Similar arguments pertain to the small solvent effect on the kinetic parameters.

Discussion of the Mechanism of Oxidatively Induced Reductive Elimination from 1 and 2. Thermal intramolecular reductive-elimination processes are usually believed to be concerted reactions. This is not necessarily a valid assumption when the reactions are oxidatively induced. A seemingly concerted reductive elimination can occur stepwise with homolytic cleavage of one bond followed by radical abstraction within the solvent cage. The groups of Fukuzumi^{3a} and Ward^{3b} have previously discussed similar situations. In their oxidations of cis-(bpy)₂CoR₂ (R = Ph, Et, Me, PhCH₂) and Cp₂MR₂ (M = Ti, Zr; R = Ph), respectively, they observed product distributions that could only be explained by the radical reaction pathway outlined above.

For a concerted reaction to occur, the ligands to be eliminated must be *cis* to each other. Homolytic cleavage, on the other hand, can give reductive-elimination reactions also with *trans* ligands. For a concerted elimination to occur from 1^{+} , an isomerization must preceed the elimination step. Thus, we cannot rule out a concerted reaction for reductive elimination of $[PhC_2]_2$ from the bis(acetylide).

PhC₂H, which is expected to be formed from 1 and 2 if radicals are formed by homolytic cleavage and escape from the solvent cage, was not observed. Still, the total absence of this product cannot be taken as evidence for a concerted reaction. As described above, efficient intracage reaction can preclude formation of phenylacetylene. Assuming that 1^+ is isomerized, the steps depicted in Scheme 9 describe the two possibilities.

A similar situation has previously been discussed for the oxidatively induced reductive elimination from Cp*Rh(PPh₃)Me₂.¹⁶ In acetonitrile it was shown to yield ethane with no trace of methane. The negative activa-



tion entropy of the reaction (-25.9 J/(K mol)) was taken as evidence for a concerted reaction with an ordered transition state. The activation entropies for 1 and 2, however, are not as informative. They were found to be 8.1 \pm 11.7 and 5.9 \pm 5.4 J/(K mol) for 1 in dichloromethane and acetonitrile, respectively, and $-6.4 \pm$ 20.1 J/(K mol) for 2 in acetonitrile. Not only are the activation entropies close to zero but the standard deviations are also rather large. Small activation entropies may result from partial cancellation of positive and negative contributions. In our experiments it is evident that solvation both of the cation radical and of the first-formed elimination product, together with the entropy of the transition state, will play a role. Thus, the exact mechanism of the coupling of the organic ligands in 1 and 2 may at the current level of understanding be well described as either a concerted or a stepwise, in-cage reaction.

The discussion above, and in particular the absence of PhC_2H , demonstrates that there is no hard evidence for products resulting from radicals released from solvent cages. Thus, the 2-3% $[PhC_2]_2$ detected in the product mixtures from the oxidation of 2 (acetonitrile and dichloromethane solvents) is probably not formed by attack of a "stray radical" on another molecule of 2. Therefore, we propose that this product is formed in a competing, inefficient bimolecular mechanism, perhaps involving a bridging acetylide ligand.

Discussion of the Mechanism of Formation of (E)- and (Z)-PhC₂CHCHPh. The discussion to follow is based on two established facts: (a) the enyne is not isomerized after generation and (b) the starting material **2** retains its *trans* stereochemistry around the vinylic double bond.

The oxidation of 2 yields a 9/1 ratio of (E)- and (Z)-PhC₂CHCHPh in acetonitrile and dichloromethane. If a concerted reductive elimination were to take place, only (E)-PhC₂CHCHPh would be produced. However, the 9/1 (E/Z) product mixture can occur from a concerted reaction with a minor (10%) competing homolytic cleavage reaction, yielding some (Z)-enyne. Homolytic cleavage itself can also give the observed ratio of stereoisomers if the radical reacts so quickly that only a small part of the radicals lose their stereochemistry.

Electrochemical methods have demonstrated that the cation radical has a half-life of several seconds. This is apparently sufficient for rearrangement via the processes shown in Scheme 10. Note especially than an η^2 -vinyl structure can lead to loss of stereochemistry

about the C=C bond while simultaneously increasing the valence-electron count at the metal; this represents a new and unusual type of 17-/19-electron interconversion.

Experimental Section

General Procedures. All manipulations involving organometallic compounds were carried out with use of vacuum line, Schlenk, syringe, or drybox techniques. Hexane was dried and deoxygenated over sodium benzophenone, acetonitrile was distilled from P_2O_5 , and acetonitrile- d_3 and dichloromethane- d_2 were distilled from CaH₂, whereas benzene- d_6 was distilled from Na and nitromethane- d_3 from CaCl₂. All solvents, PhC₂H, and (p-tolyl)C₂H were subjected to three freeze-pump-thaw cycles at the vacuum line prior to use. Acetonitrile and dichloromethane containing the supporting electrolyte were passed through a column of active neutral alumina prior to use to remove water and protic impurities before electrochemical measurements. The electrolyte was freed of air by purging with purified argon, and all measurements and electrolyses were carried out under a blanket of solvent-saturated argon.

Electrochemical measurements were performed with an EG&G-PAR Model 273 potentiostat/galvanostat driven by an external HP 3314 sweep generator. The output signals were fed to a Nicolet 310 digital oscilloscope and processed by an on-line personal computer. The working electrode was a Pt-disk electrode (d = 0.6 mm), the counter electrode was a Pt wire, and the Ag-wire reference electrode assembly²⁹ was filled with acetonitrile/0.01 M AgNO₃/0.1 M Bu₄N(PF₆). The reference electrode was calibrated against Cp₂Fe, which is used as the reference in this work. The positive-feedback *iR* compensation circuitry of the potentiostat was employed; the separation between the anodic and cathodic peaks for the Cp₂Fe oxidation was 59–61 mV in acetonitrile.

Hydrocarbons were separated and quantified on a Varian 3400 GC using a 25 m DB5 column.

¹H (referenced via residual solvent protons) and ¹³C (referenced to the solvent resonance) NMR and ¹⁹F (referenced to CFCl₃) NMR spectra were recorded on a Varian XL-300 instrument. The symbol vt in ¹H NMR spectra denotes virtual triplets arising from coupling to magnetically nonequivalent P nuclei. ³¹P{¹H} (referenced to 85% H₃PO₄) NMR was recorded on a a Varian XL-300 instrument or a Nicolet NT-360 spectrometer operating at 121 or 146 MHz, respectively. ¹H{³¹P} NMR spectra were obtained on a Nicolet NT-360 spectrometer. Infrared spectra were recorded in benzene-*d*₆, acetonitrile-*d*₃, or dichloromethane-*d*₂ (NaCl cavity cell, 0.1 mm path length) on a Nicolet 510P FT-IR spectrometer with a precision of 0.3 cm⁻¹.

The compounds $[Cp_2Fe]PF_6,^{30a}$ $[(\eta^5-C_5H_4COMe)CpFe]BF_4$ (AcFc(BF₄)),^{30b} Ru(C₂Ph)₂(CO)(P^tBu₂Me)₂¹¹ (1), and (*E*)-PhC₂-CHCHPh²⁴ were prepared according to published procedures. All other compounds were used as received from commercial suppliers.

Ru(CHCHPh)(C₂Ph)(CO)(PⁱBu₂Me)₂ (2). This is a modification of a previously published procedure.¹¹ Ru(H)(Cl)(CO)(P^t-Bu₂Me)₂ (400 mg, 0.82 mmol) was added to hexane (20 mL) and PhC₂H (90 μ L, 0.82 mmol) and stirred for 15–20 min. PhC₂Li (178 mg, 1.64 mmol) was added. The resulting mixture was stirred for 6 h, filtered, and concentrated to approximately 4 mL. The filtrate was stored at -20 °C for 24 h, during which time the product crystallized as a dark red solid (365 mg, 68% yield). ¹H NMR (300 MHz, benzene-d₆): δ 1.13 (vt, J = 5.9 Hz, 18 H), 1.21 (vt, J = 5.9, 18 H), 1.52 (s, 6 H), 6.26 (d, J = 13 Hz, 1 H), 6.9–7.7 (m, 10 H), 8.62 (d, J = 13 Hz, 1 H). ³¹P-

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{¹H} NMR (146 MHz, benzene- d_6): δ 40.9 (s). IR (benzene- d_6): $v_{\rm CO}$ 1910 cm⁻¹, $v_{\rm CC}$ 2074 cm⁻¹.

X-ray Structure Determination of Ru(C.Ph)₂(CO)- $(\mathbf{P}^{\mathsf{t}}\mathbf{Bu}_{2}\mathbf{Me})_{2}$ (1). Because of the slow onset of a phase transition at -167 °C, we undertook a study at -90 °C, where a systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic (2/m)diffraction symmetry. The only observed extinction was that of 0k0 for k = 2n + 1, leading to the choice of the possible space group $P2_1$ or $P2_1/m$. The choice of the noncentrosymmetric space group $P2_1$ was based on the fact that the structure could be solved using $P2_1$ but not $P2_1/m$. Unit cell dimensions were determined by a least-squares fit of the setting angles for 62 carefully centered reflections having 2 values between 20 and 34°. Following the usual data reduction and averaging of equivalent data, a unique set of 2322 reflections was obtained. The R values for the averaging was 0.113 for 2293 reflections observed more than once. Plots of the 4 standard reflections (-3,0,0, -3,3,3, 0, -6,0, 0,0,4) measured every 300 reflections showed no significant trends. No correction for absorption was performed. The structure was solved using SHELXS-86. While the Ru and P atoms as well as the CO group and the two C₂Ph groups were readily located, the substituents on the phosphorus caused considerable difficulty. A relatively good model could be obtained but would not be refined in a satisfactory manner. The final least-squares refinement was carried out using anisotropic thermal parameters on the Ru and P atoms and isotropic parameters on the remaining atoms. For the refinement, only 1193 reflections considered observed by the criterion $F > 3.0\sigma(F)$ were used. For the disordered carbon atoms in the phosphine ligands, occupancies were refined initially and then fixed. The isotropic thermal parameters for all of the atoms are quite high, an indication that the data might have been collected close to the transition temperature or that the structure is very disordered. The largest peaks in the final difference map were 0.78 e/A^3 and revealed that smaller residuals were located in the area of the disordered carbon atoms. Because of some relatively large esd's (e.g., Ru-C20 = 2.05(8) Å) and an unreasonable angle $(Ru-C20-O21 = 143(5)^\circ)$, we furnish full structural details only in the supplementary material. A view of the molecule and some selected metric parameters are shown in Figure 1 and Table 1.

Coordination of Acetonitrile to \operatorname{Ru}(C_2\operatorname{Ph})_2(\operatorname{CO}) (P^tBu₂Me)₂ (1). $\operatorname{Ru}(C_2\operatorname{Ph})_2(\operatorname{CO})(\operatorname{Pt}\operatorname{Bu}_2\operatorname{Me})_2$ (1; 20.0 mg, 0.03 mmol) dissolved in benzene- d_6 was added to an NMR tube. The ³¹P NMR spectrum of the compound showed a single resonance at δ 47.7. Acetonitrile (1.5 μ L, 1 equiv) was added to the solution, whereupon the color immediately changed from dark red to bright yellow. The ³¹P{¹H} NMR spectrum showed only one signal (at δ 45.3). Addition of excess acetonitrile (3 \times 15 μ L) gave no change in either the shift of the peak or the color of the solution. The IR absorptions changed from ν_{CO} 1933 cm⁻¹ and ν_{CC} 2074 cm⁻¹ in neat benzene- d_6 to ν_{CO} 1934 cm⁻¹ and ν_{CC} 2082 cm⁻¹ in the benzene- d_6 /acetonitrile solvent mixture.

 $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (20.0 mg, 0.031 mmol) was dissolved in acetonitrile (2 mL). This gave a yellow solution, from which a pale yellow solid precipitated immediately. The solid was collected. A sample was analyzed by ³¹P{¹H} NMR spectroscopy in benzene- d_6 . It showed the same resonance as above, δ 45.3. The rest of the solid was dried in vacuo overnight. This yielded a red solid which was shown to be $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (³¹P{¹H} NMR, benzene- d_6).

The solid that precipitated from acetonitrile solutions of $\operatorname{Ru}(C_2\operatorname{Ph})_2(\operatorname{CO})(\operatorname{Pt}\operatorname{Bu}_2\operatorname{Me})_2$ was dried 2-3 min in vacuo and analyzed by ¹H NMR spectroscopy in benzene- d_6 . A signal was present at δ 0.62 (in addition to the usual resonances for 1). Upon addition of 10 μ L of acetonitrile- d_3 , this peak moved to δ 0.69.

Coordination of Acetonitrile to $Ru(CHCHPh)(C_2Ph)$ -(CO)(P^tBu₂Me)₂ (2). An NMR tube was prepared containing Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂Me)₂ (**2**; 20.0 mg, 0.03 mmol) dissolved in benzene- d_6 . A ³¹P{¹H} NMR spectrum showed the phosphine resonance at δ 42.4. Addition of acetonitrile (1.5 μ L, 1 equiv) gave no apparent color change and no change in the position of the phosphine resonance. Addition of excess acetonitrile (15 μ L) resulted in the appearance of a weak resonance at δ 45.0. More acetonitrile (2 × 15 μ L) was added upon which the small resonance gained somewhat in intensity (ca. 5% of the intensity of the main resonance) and the dark red color faded perceptibly. After addition of 47 μ L of acetonitrile, the solution was red-orange. The IR (benzene- d_6) absorptions (ν_{CO} 1910 cm⁻¹ and ν_{CC} 2074 cm⁻¹) did not change when acetonitrile was added, but a small shoulder (ca. 5%) appeared at higher frequency on the CO peak.

 $\label{eq:rescaled} \begin{array}{l} Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)_2 \ (20.0 \ mg, \ 0.03 \ mmol) \\ was dissolved in acetonitrile (2 \ mL). This gave a red-orange solution, from which a red solid precipitated immediately. The solid was dried in vacuo overnight. This yielded a red solid, which was shown to be Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)_2 \ by \ ^{31}P\{^{1}H\} \ NMR \ spectroscopy \ in \ benzene-d_{6}. \end{array}$

The solid that precipitated from acetonitrile solutions of Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂Me)₂ was dried for only 2–3 min in vacuo and analyzed by ¹H NMR spectroscopy in benzene- d_6 . A signal was present at δ 0.59 (in addition to the usual resonances for 2). Upon addition of 10 μ L of acetonitrile- d_3 , the peak moved to δ 0.71.

Thermal Reactions of 1 and 2. $\operatorname{Ru}(\operatorname{C_2Ph})_2(\operatorname{CO})(\operatorname{PtBu_2Me})_2$ (10.0 mg, 0.02 mmol) was dissolved in benzene- d_6 and added to an NMR tube equipped with a ground-glass joint. The NMR tube was flame-sealed under vacuum, and a ¹H NMR spectrum was acquired. A similar sample of Ru(CHCHPh)(C_2Ph)(CO)-(PtBu₂Me)₂ (10.0 mg, 0.02 mmol) in benzene- d_6 was prepared. The samples were heated at 50 °C for 24 h. No change occurred in the NMR spectra of the samples. Further heating of the samples at 74 °C for 24 h generated traces (ca. 5%) of free PtBu₂Me (¹H NMR (300 MHz, benzene- d_6) δ 1.04 (d, J =10.5 Hz), 0.82 (d, J = 4.3)). Further heating (for 48 h) only yielded more of the phosphine. ³¹P NMR spectroscopy confirmed that PtBu₂Me was the only detectable product from the reactions (³¹P{¹H} NMR (146 MHz, benzene- d_6) δ 11.8 ppm).

General Procedure: Oxidation of 1 in Acetonitrile. In a typical experiment Ru(C₂Ph)₂(CO)(P^tBu₂Me)₂ (1; 20.0 mg, 0.03 mmol) was dissolved in acetonitrile (25 mL) and slowly added to a solution of AcFc(BF₄) (19.3 mg, 0.06 mmol) in acetonitrile (5 mL). The solvent was stripped off from the yellow solution, and the residue was dissolved in acetonitrile d_3 and analyzed by ¹H and ³¹P{¹H} NMR and IR spectroscopy. ¹H NMR (300 MHz, acetonitrile- d_3): δ 1.40 (vt, J = 7 Hz, 36 H), 1.53 (vt, J = 3 Hz, 6 H), 6.9–7.2 (m), 7.3–7.7 (m). ³¹P-{¹H} NMR (146 MHz, acetonitrile- d_3): δ 40.5 (s), 42.4 (s), 60.1 (s). IR (acetonitrile- d_3): ν_{CO} 2010 cm⁻¹.

The solution from the NMR tube was added to ether (20 mL) and filtered. The solid was dried under vacuum, dissolved in acetonitrile- d_3 , and analyzed by ¹H and ³¹P{¹H} NMR spectroscopy. The solvent was stripped off from the filtrate, and the residue was dried and dissolved in acetonitrile- d_3 . Analysis by NMR spectroscopy gave the following. Residue: ¹H NMR (300 MHz, acetonitrile- d_3) δ 1.40 (vt, J = 7 Hz, 36 H), 1.53 (vt, J = 3 Hz, 6 H); ³¹P{¹H} NMR (146 MHz, acetonitrile- d_3) δ 40.5 (s), 42.4 (s); IR (acetonitrile- d_3) ν_{CO} 2010 cm⁻¹. Filtrate: ¹H NMR (300 MHz, acetonitrile- d_3) δ 7.3–7.7 (m, 10 H); ¹³C{¹H} NMR (75 MHz, acetonitrile- d_3) 74.1, 82.4, 122.1, 129.7, 130.7, 133.4; MS m/e 202.

Oxidation of 2 in Acetonitrile. The oxidation was done as in the general procedure described above. Spectroscopic data before workup are as follows. ¹H NMR (300 MHz, acetonitrile- d_3): δ 1.40 (vt, J = 7 Hz, 36 H), 1.53 (vt, J = 3 Hz, 6 H), 6.0 (d, J = 12.1 Hz, 1 H), 6.57 (d, J = 16.5 Hz, 1 H), 6.83 (d, J = 12.1 Hz, 1 H), 7.36 (d, J = 16.5, 1 H), 7.2–8.0 (m, 10 H). ³¹P{¹H} NMR (146 MHz, acetonitrile- d_3): δ 42.4 (s). IR (acetonitrile- d_3): ν_{CO} 2010 cm⁻¹. Spectroscopic data after workup are as follows. Residue: ¹H NMR (300 MHz, acetonitrile- d_3) δ 1.40 (vt, J = 7 Hz, 36 H), 1.53 (vt, J = 3 Hz, 6 H); ³¹P{¹H} NMR (146 MHz, acetonitrile- d_3) δ 42.4 (s); IR (acetonitrile- d_3) ν_{CO} 2010 cm⁻¹. Filtrate: ¹H NMR (300 MHz, acetonitrile- d_3) δ 6.00 (d, J = 12.1 Hz, 1 H), 6.57 (d, J = 16.5Hz, 1 H) 6.83 (d, J = 12.1 Hz, 1 H), 7.36 (d, J = 16.5, 1 H), 7.2–8.0 (m, 15 H); MS m/e 204.

General Procedure: Oxidation of 1 in Dichloromethane. In a typical experiment, $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (1; 20.0 mg, 0.03 mmol) was dissolved in dichloromethane (5 mL) and slowly added to a solution of AcFc(BF₄) (19.3 mg, 0.06 mmol) in dichloromethane (2 mL). The solvent was stripped off from the purple solution; the residue was dissolved in dichloromethane- d_2 and the solution analyzed by ¹H and ³¹P-{¹H} NMR spectroscopy. ¹H NMR (300 MHz, dichloromethane- d_2): δ 1.30 (d, J = 16.8 Hz, 36 H), 1.45 (dd, J = 13.4 and 5.5 Hz, 6 H), 7.3-7.6 (m, 10 H). ³¹P{¹H} NMR (146 MHz, dichloromethane- d_2): δ 39.9 (s), 41.9 (s), 72.8 (s), 73.9 (s), 76.8 (s). IR (dichloromethane- d_2): ν_{CO} 1951 cm⁻¹.

The solution from the NMR tube was added to ether (20 mL), and the resulting solid was filtered. The solid was dried under vacuum, dissolved in dichloromethane- d_2 , and analyzed by ¹H and ³¹P{¹H} NMR spectroscopy. The solvent was stripped off from the filtrate, and the residue was dried and dissolved in dichloromethane- d_2 . Residue: ¹H NMR (300 MHz, dichloromethane- d_2) δ 1.49 (d, J = 16.8 Hz, 36 H), 1.85 (dd, J = 13.4 and 5.5 Hz, 6 H); ¹H{³¹P} NMR (300 MHz, dichloromethane- d_2) δ 1.30 (s, 36 H), 1.45 (br s, 6 H); ³¹P{¹H} NMR (146 MHz, dichloromethane- d_2) δ 39.9 (s); ¹⁹F NMR (55 MHz, dichloromethane- d_2) δ -150.7 (br s); IR (dichloromethane- d_2) ν_{CO} 1951 cm⁻¹. Filtrate: ¹H NMR (300 MHz, dichloromethane- d_2) δ 7.34–7.45 (m), 7.53–7.60 (m); ¹³C (75 MHz, dichloromethane- d_2) δ 73.9, 81.8, 122.0, 128.9, 129.7, 132.8; MS m/e 202.

Oxidation of 2 in Dichloromethane. The oxidation was done as in the general procedure described above. Spectroscopic data before workup are as follows. ¹H NMR (300 MHz, dichloromethane- d_2) δ 1.30 (d, J = 16.8 Hz, 36 H), 1.45 (dd, J= 13.4 and 5.5 Hz, 6 H), 5.92 (d, J = 12.1 Hz, 1 H), 6.39 (d, J= 16.5 Hz, 1 H), 6.71 (d, J = 12.1 Hz, 1 H), 7.15 (d, J = 16.5, 1 H) 7.2-8.0; ³¹P{¹H} NMR (146 MHz, dichloromethane- d_2) δ 39.9 (s); IR (dichloromethane- d_2): ν_{CO} 1951 cm⁻¹. Spectroscopic data after workup are as follows. Residue: ¹H NMR (300 MHz, dichloromethane- d_2) δ 1.30 (d, J = 16.8 Hz, 36 H), 1.45 (dd, J = 13.4 Hz, 6 H); ³¹P{¹H} NMR (146 MHz, dichloromethane- d_2) δ 39.9 (s); IR (dichloromethane- d_2): v_{CO} 1951 cm⁻¹. Filtrate: ¹H NMR (300 MHz, dichloromethane d_2) δ 5.92 (d, J = 12.1 Hz, 1 H), 6.39 (d, J = 16.5 Hz, 1 H), 6.71 (d, J = 12.1 Hz, 1 H), 7.15 (d, J = 16.5, 1 H), 7.2-8.0; MSm/e 204.

The residue from the oxidation of Ru(CHCHPh)(C₂Ph)(CO)-(P^tBu₂Me)₂ in dichloromethane was dissolved in acetonitrile d_3 . The resulting mixture contained mostly the dicationic acetonitrile adduct [Ru(CO)(NCMe)₃(P^tBu₂Me)₂](BF₄)₂ (ca. 80% by inspection of the ³¹P{¹H} NMR spectrum).

Ru[**C**₂(**p-tolyl**)]₂(**CO**)(**P**^t**Bu**₂**Me**)₂. Ru(H)(Cl)(CO)(P^tBu₂-Me)₂ (300.0 mg, 0.62 mmol) was added to hexane (35 mL) and (p-tolyl)C₂H (0.3 mL, 4 equiv) and (p-tolyl)C₂Li (96.0 mg, 0.79 mmol). The resulting mixture was refluxed for 12 h, filtered, and concentrated to approximately 5 mL. This solution was filtered to remove an insoluble byproduct. The filtrate was stored at -20 °C for 24 h, and the product crystallized as a dark red solid (207 mg, 49%). ¹H NMR (300 MHz, benzene-d₆): δ 1.32 (vt, 36 H), 1.79 (vt, 6H), 2.13 (s, 6 H), 7.10 (d, 4H), 7.56 (d, 4 H); ³¹P{¹H} NMR (360 MHz, benzene-d₆) δ 47.9 (s); IR (benzene-d₆) ν_{CO} 1931 cm⁻¹, ν_{CC} 2077 cm⁻¹.

Oxidation of Ru[C₂(*p*-tolyl)]₂(CO)(P^tBu_2Me)₂ in Acetonitrile and Dichloromethane. The oxidation of Ru[C₂(*p*tolyl)]₂(CO)(P^tBu_2Me)₂ in acetonitrile and dichloromethane was done as described in the general procedures for the oxidations of 1 and 2. In acetonitrile the dicationic acetonitrile adduct [Ru(CO)(NCMe)₃(P^tBu_2Me)₂](BF₄)₂ (¹H and ³¹P{¹H} NMR and IR spectroscopy) was formed together with an ether-soluble product. Oxidation in dichloromethane gave a mixture of organometallic products that closely resembled the product mixtures obtained when $\text{Ru}(\text{C}_2\text{Ph})_2(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$ and $\text{Ru}(\text{CHCHPh})(\text{C}_2\text{Ph})(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$ were oxidized in dichloromethane (by ¹H and ³¹P NMR and IR spectroscopy). Extraction with ether as in the general procedure yielded an extract with the following spectroscopic data: ¹H NMR (300 MHz, benzene- d_6) δ 1.90 (s, 6 H), 6.5–7.4 (m, 10 H); MS m/e 230.

[Ru(CO)(NCMe)₃(PtBu₂Me)₂](BF₄)₂ (3). Ru(C₂Ph)₂(CO)-(PtBu₂Me)₂ (20.0 mg, 0.03 mmol) was dissolved in acetonitrile (25 mL) and slowly added to a stirred solution of AcFc(BF₄) (19.3 mg, 0.06 mmol) in acetonitrile (5 mL). This gave a yellow solution. The solution was concentrated to 2-3 mL and added to ether (20 mL). Filtration of the solution yielded a gray solid which was dissolved in acetonitrile and recrystallized by diffusion of ether vapor into the acetonitrile solution. ¹H NMR (300 MHz, acetonitrile- d_3): δ 1.40 (vt, J = 7 Hz, 36 H), 1.53 (vt, J = 3 Hz, 6 H), 2.49 (s, 6 H), 2.58 (s, 3 H); this spectrum was taken within 7 min of warming a freshly prepared frozen (-196 °C) sample to 25 °C, to minimize exchange of MeCN trans to CO with bulk CD₃CN. ¹H NMR (300 MHz, nitromethane- d_3): δ 1.49 (vt, J = 7 Hz, 36 H), 1.65 (vt, J = 3 Hz, 6 H), 2.64 (s, 6 H), 2.71 (t, J = 1.1 Hz, 3 H). ³¹P{1H} NMR (121 MHz, acetonitrile- d_3): δ 42.4 (s). ¹³C{¹H} NMR (75 MHz, acetonitrile-d₃): δ 5.8, 30.0 (d), 37.7 (t), 131.0, 134.5, 201.4 (t). IR (acetonitrile- d_3): $v_{\rm CO}$ 2010 cm⁻¹

Investigation of the Molecularity of the Reductive Elimination from 1. A solution of $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (20.0 mg, 0.03 mmol) and $Ru[C_2(p-tolyl)]_2(CO)(P^tBu_2Me)_2$ (20.7 mg, 0.03 mmol) in acetonitrile (50 mL) was slowly added to an acetonitrile solution (5 mL) of $AcFc^+(BF_4^-)$ (38.6 mg, 0.12 mmol). The reaction mixture was concentrated to 1–2 mL, added to ether (30 mL), and filtered through Celite.

A dark brown oil was obtained from the filtrate. The oil contained only $[PhC_2]_2$ and $[(p-tolyl)C_2]_2$ by ¹H NMR spectroscopy. Mass spectrometry showed parent ions at m/e 202 ($[PhC_2]_2$) and 230 ($[(p-tolyl)C_2]_2$). The crossover product, (p-tolyl)C₂-C₂Ph, was not obtained in either solvent.

The experiment was repeated with dichloromethane as the solvent. This gave, as for the reaction in acetonitrile, only formation of $[PhC_2]_2$ and $[(p-tolyl)C_2]_2$.

Identification of the Products from the Oxidation of 2. A solution of Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂Me)₂ (2) was oxidized with AcFc(BF₄) as described in the general procedure for oxidation reactions. The reaction mixture was concentrated to 1-2 mL, added to ether (30 mL), and filtered through Celite.

Dark brown oils were obtained from the filtrates of reactions in both acetonitrile and dichloromethane. The oils were dissolved in 0.5 mL of benzene and analyzed by capillary GLC. Authentic samples of $[PhC_2]_2$ and $PhC_2CHCHPh$ were used to determine the retention times. Oxidation of Ru(CHCHPh)- $(C_2Ph)(CO)(P^tBu_2Me)_2$ in acetonitrile showed formation of 97% $PhC_2CHCHPh$ and 3% $[PhC_2]_2$. Oxidation of $Ru(CHCHPh)(C_2-Ph)(CO)(P^tBu_2Me)_2$ in dichloromethane showed formation of 97.5% of $PhC_2CHCHPh$ and 2.5% of $[PhC_2]_2$. There was no evidence for formation of PhC_2H .

NMR Quantification of the Yield of the Organometallic Product from the Oxidation of 1. A solution of $Ru(C_2-Ph)_2(CO)(P^tBu_2Me)_2$ (1; 30.0 mg, 0.05 mmol) and hexamethylbenzene (HMB; 7.4 mg, 0.05 mmol) was dissolved in dichloromethane (3 mL). The solution was distributed equally into three different flasks. The solution from one flask was slowly added to a solution of $AcFc(BF_4)$ (9 mg, 0.03 mmol) in dichloromethane. The solvent was stripped off from the second flask at -20 °C; the residue was dissolved in acetonitrile (15 mL) and this solution slowly added to a solution of $AcFc(BF_4)$ (0.09 mg, 0.03 mmol) in acetonitrile (3 mL). The solvents from each flask were now stripped off at -20 °C. The residues were analyzed by ¹H NMR spectroscopy.

The yields of product from the reactions in acetonitrile and dichloromethane were established by comparison with the internal standard (HMB). In acetonitrile, the yield of [Ru- $(CO)(P^tBu_2Me)_2(NCMe)_3](BF_4)_2$ was found to be 72%. In dichloromethane, the yield of main product was 52%.

Quantification of the Yield of the Organic and the Organometallic Product from the Oxidation of 2. (a) By NMR. The experiment was done as described above. In acetonitrile the yield of $[Ru(CO)(NCMe)_3(P^tBu_2Me)_2](BF_4)_2$ was 75% and the yield of PhC₂CHCHPh was 70%. In dichloromethane the yield of the main organometallic product was 42%, whereas 46% PhC₂CHCHPh was formed.

(b) By GC. $Ru(CHCHPh)(C_2Ph)(CO)(P^tBu_2Me)_2$ (2; 20.0 mg, 0.03 mmol) was oxidized with $AcFc(BF_4)$ (19.3 mg, 0.06 mmol) in acetonitrile and in dichloromethane as described in the general procedures. After workup of the reaction mixtures, the solvents of the filtrates were evaporated in vacuo. The residues were dissolved in benzene (0.5 mL) and analyzed by capillary GLC. Solutions of PhC₂CHCHPh (7.4 mg, 0.04 mmol; 5.8 mg, 0.03 mmol; 3.7 mg, 0.02 mmol; 1.9 mg, 0.01 mmol) in benzene (0.5 mL) were also analyzed by GLC. This allowed determination of the yield of PhC₂CHCHPh from the oxidation reactions. The amount of PhC₂CHCHPh formed in the oxidation in acetonitrile and dichloromethane was 59% and 40%, respectively. From the quantification of the yield of PhC₂-CHCHPh in the oxidation of 2 by means of ¹H NMR spectroscopy, it is possible to estimate the loss during workup of the reaction mixtures to be ca. 10%.

GC Quantification of the Yield of the Organic Product from the Oxidation of 1. $Ru(C_2Ph)_2(CO)(P^tBu_2Me)_2$ (1; 20.0 mg, 0.03 mmol) was oxidized with AcFc(BF₄) (19.3 mg, 0.06 mmol) in acetonitrile and in dichloromethane as described in the general procedures. After workup of the reaction mixtures, the solvents of the filtrates were evaporated in vacuo. The residues were dissolved in benzene (0.5 mL) and analyzed by capillary GLC. Solutions of [PhC2]2 (6.7 mg, 0.03 mmol; 4.6 mg, 0.02 mmol; 3.1 mg, 0.015 mmol; 1.5 mg, 0.007 mmol) in benzene (0.5 mL) were also analyzed by GLC. This allowed determination of the yield of [PhC2]2 from the oxidation reactions. The amounts of $[PhC_2]_2$ formed in the oxidations in acetonitrile and dichloromethane were 62% and 39%, respectively. From the quantification of the yield of PhC₂-CHCHPh in the oxidation of 2 by means of both ¹H NMR and GLC, it is possible to estimate the loss during workup of the reaction mixtures to be ca. 10%.

Attempted E/Z Isomerization of the -CHCHPh Ligand in 2 by AcFc(BF₄). Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂Me)₂ (20.0 mg, 0.03 mmol) was oxidized by AcFc(BF₄) (3.8 mg, 0.022 mmol, 0.4 equiv). Two reactions were performed, one in acetonitrile and one in dichloromethane. The oxidations and the workup were done as described before. In acetonitrile only resonances for [Ru(CO)(NCMe)₃(P^tBu₂Me)₂](BF₄)₂, (E)-PhC₂-CHCHPh, and unconsumed Ru(CHCHPh)(C₂Ph)(CO)(P^tBu₂-Me)₂ were present in the ¹H NMR spectrum, in addition to The same result was obtained when dichloromethane was used as solvent.

Attempted E/Z Isomerization of (E)-PhC₂CHCHPh by AcFc-(BF₄). (E)-PhC₂CHCHPh (10.0 mg, 0.005 mmol) and AcFc-(BF₄) (4.2 mg, 0.013 mmol) were dissolved in dichloromethane d_2 and added to a NMR tube equipped with a ground-glass joint. The tube was sealed and a ¹H NMR spectrum was recorded. No isomerization of (E)-PhC₂CHCHPh to (Z)-PhC₂-CHCHPh occurred (¹H NMR spectroscopy) over 36 h.

Attempted Isomerization of (E)-PhC₂CHCHPh by Oxidation Products. (E)-PhC₂CHCHPh (10.0 mg, 0.005 mmol) and the products from an oxidation of $Ru(C_2Ph)_2(CO)(P^tBu_2-Me)_2$ (1) in dichloromethane were dissolved in dichloromethane d_2 , and this solution was added to a NMR tube equipped with a ground-glass joint. The tube was sealed, and a ¹H NMR spectrum was recorded. No isomerization of (E)-PhC₂CHCHPh to (Z)-PhC₂CHCHPh occurred (¹H NMR spectroscopy) over 36 h.

Constant-Current Coulometry. The constant-current electrolyses were performed in an H-shaped cell, the compartments of which were separated by a medium-frit glass junction. A platinum-gauze working electrode was used. Solutions of 1 and 2 (1-2 mM) in 20 mL of acetonitrile with 0.05 M Me₄N-(BF₄) as the supporting electrolyte were electrolyzed with a constant current of 10 mA, while the consumption of substrate was monitored by DCV. Three separate measurements indicated the consumption of 2.0 ± 0.1 faradays/mol of charge for both 1 and 2. In dichloromethane/0.2 M Bu₄N(PF₆), 1.3 and 1.5 faradays/mol were consumed for 1 and 2, respectively.

The solution obtained by electrolysis of 1 in acetonitrile was concentrated. A sample of the resulting mixture was analyzed by ³¹P{¹H} NMR spectroscopy. This showed formation of $[Ru(CO)(NCMe)_3(P^tBu_2Me)_2](BF_4)_2$ as the major product (ca 90% of total signal intensity). The same was found for the constant-current electrolysis of 2 in acetonitrile.

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Supplementary Material Available: Tables of crystallographic data, fractional coordinates, thermal parameters, and bond distances and angles (6 pages). Ordering information is given on any current masthead page.

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