

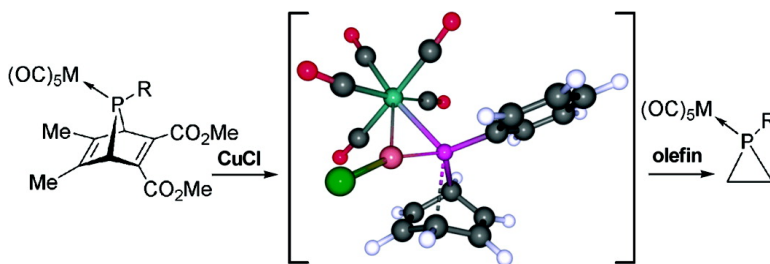
Article

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Copper(I) Chloride Initiated Decomposition of 7-Phosphanorbornadiene. Evidence for a Solvent-Assisted Catalytic Mechanism

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Abstract: Density functional theory is used to explore the mechanism of the copper(I)-chloride-catalyzed decomposition of $W(CO)_5$ -complexed 7-phosphanorbornadiene and the subsequent olefin trapping of the terminal phosphinidene complex. CuCl lowers the activation barrier by interacting directly with the breaking P–C bond. Contrary to the prevailing notion that a free terminal phosphinidene complex ($W(CO)_5=PR$) is generated in the CuCl-catalyzed cheletropic elimination of the 7-phosphanorbornadiene– $W(CO)_5$ complex, the present mechanism suggests that CuCl is attached to the terminal phosphinidene. Furthermore, a “chloride shuttle” takes place where the chloride first migrates to the phosphorus center and then is returned back to the copper center by the incoming olefin in an S_N2 reaction step. When the substituent on phosphorus is a phenyl group ($R = Ph$), the uncatalyzed reaction has an activation barrier of 17.9 kcal/mol, which is reduced by 10.9 kcal/mol on including the CuCl catalyst. The CuCl-catalyzed decomposition of 7-phosphanorbornadiene followed by olefin trapping of the terminal phosphinidene complex has a close parallel with the Cu(I)-catalyzed cyclopropanation reaction of diazoalkane. In both catalyzed reactions, copper(I) is coordinated to the phosphinidene/carbene as a Lewis acid, while a Lewis base is displaced from the phosphorus/carbon center as the olefin is added.

Introduction

The chemistry of phosphinidenes, both with and without transition metal groups, is a topic of current interest. While free mesitylphosphinidene¹ was reportedly detected by EPR spectroscopy in 1994 and phenylphosphinidene (PPh) was detected 5 years later by mass spectrometry in a neutralization-reionization experiment,² the chemistry is much more vibrant for the terminal-complexed species in which the transition metal group controls the reactivity of the phosphinidene.^{3–5} For example, those with electrophilic properties add/insert to/into various bonds (i.e., CC, CSi, CN, CH, NH, OH, ...) to produce a diversity of compounds.^{6,7} Their reactivity resembles that of the carbenes, which stems from the comparable electronegativities

of phosphorus and carbon (P 2.2, C 2.5). Yet, also nucleophilic species are feasible. The nature of a phosphinidene is readily determined by examination of its transition metal group. With σ -donating ligands on the transition metal, the electron density on the phosphorus atom is increased ($M^{\delta+}\cdots P^{\delta-}$) and the

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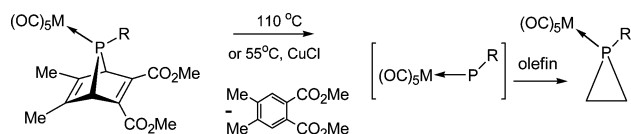


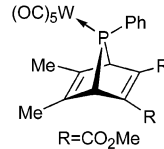
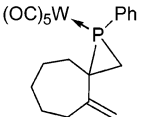
Figure 1. Decomposition of 7-PNBD with olefin addition.

complex behaves nucleophilically (Schrock), whereas π -acceptor ligands reduce the charge on phosphorus ($M^{\delta-}\cdots P^{\delta+}$), resulting in an electrophilic complex (Fischer).⁸ While the terms Schrock/Fischer were coined for nucleophilic/electrophilic transition metal carbenes, their use for phosphinidenes is justified by their similar behavior. Many stable crystalline nucleophilic phosphinidene complexes are known for a variety of transition metals and ligands.^{9,10} For the electrophilic species, this is not the case. Their existence is inferred only from trapping experiments.^{6,7} The most employed electrophilic terminal phosphinidene complex ($(OC)_5M=PR$, $M = W, Mo, Cr$) is thermally generated, and used in situ, by cheletropic elimination from the 7-phosphanorbornadiene complex (7-PNBD) with the formation of the aromatic fragment as the thermodynamic driving force (Figure 1). Interestingly, this process is influenced by the presence of a catalytic amount of copper(I) chloride, which reduces the reaction temperature for generating $(OC)_5W=PPh$ from about 100–110 to 55 °C or below.^{6,7} The origin of the influence by CuCl is not known. Does CuCl merely facilitate the cheletropic elimination, or does it impact the nature of the phosphinidene complex?

In the chemistry of carbenes, a fundamental and recurrent question is whether the carbene is “free” or whether it is still associated to the fragment molecule.¹¹ Particularly in the case of their photolytic generation from diazo ($R_2C=N_2$) or diazirine precursors, the reactant may in fact not be completely free. Thus, distinguishing between the reactivity of the free carbene and the carbene–nitrogen complex is difficult.¹¹ In the present study,

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Table 1. Experimental Kinetic Activation Parameters, ΔH^\ddagger (kcal/mol) and ΔS^\ddagger (cal/mol·K), for Decomposition (A) and Rearrangement (B)

	ΔH^\ddagger	ΔS^\ddagger
A		
		
uncatalyzed	33.0 ^a	0.6±1.0 ^b
CuCl-catalyzed	14.3 ^c	-31.3 ^c
B		
		
uncatalyzed ^d	29.9	-0.2
CuCl-catalyzed ^e	19.2	-23.9

^a Reference 13b. ^b Derived from data in ref 13b. ^c Reference 13a. ^d Reference 14. ^e A unimolecular reaction was assumed (see text).

we raise a similar question in terms of the active species in the CuCl-catalyzed decomposition of 7-PNBD. Is a free terminal phosphinidene complex generated?

While the products for the uncatalyzed and CuCl-catalyzed reactions are usually the same, they differ in some cases. For example, reaction of 7-PNBD ($M = W$) with phospholene at 25–55 °C in the presence of CuCl gives an intermediate whose X-ray structure revealed a $P-Cu_2Cl_2-P$ core, implicating the involvement of CuCl.¹² Kinetic parameters have been reported for two reactions that illustrate the importance of CuCl (Table 1).^{12,13} For example, it was shown that CuCl reduces the activation barrier for the thermal decomposition of 7-PNBD by 18.7 kcal/mol (entry A). Also, the activation barrier for the 1,3-sigmatropic shift of vinylphosphiranes to the corresponding 1,4-adducts is reduced by 10.7 kcal/mol on using a catalytic amount of CuCl (entry B). Perhaps the most interesting feature of the CuCl-catalyzed process is its negative entropy of activation.¹⁴ Both reactions (A and B) were initially analyzed in terms of first-order processes, based on monitoring the disappearance of the phosphinidene precursor 7-PNBD, despite the negative ΔS^\ddagger . However, we now believe the CuCl-catalyzed reaction to be a second-order process that involves a CuCl–solvent complex.

Computational Method

The Gaussian 98 program system¹⁵ was used for all calculations. Geometries were optimized with the B3LYP combination of exchange and correlation functionals with effective core potentials for Cu¹⁶ and W¹⁷ and a 8s7p6d–6s5p3d basis set for the valence electrons (keyword = SDD) and a 6-31G(d) basis set for all other elements. Geometries

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were optimized within the indicated point group, and vibrational frequencies were calculated. For transition states, the vibrational frequencies were animated with the MOLDEN program.¹⁸ When the identities of the corresponding reactant and product were not clear, the transition state geometry was altered along one of the transition vectors and the geometry was optimized toward a minimum.

The total energies, zero-point energies, and related data are given for the structures considered in Table S1 (Supporting Information). All species with the same molecular formula are given a boldface capital letter designation with a number to distinguish different structures. A prime or double prime is used to distinguish closely related structures. Structures on the 7-PNBD (R = Ph) potential energy surface are given the same letter and number as the corresponding structure on the 7-PNBD (R = H) PES with a boldfaced “Ph” appended to the notation. Molecular plots of structures not given in the text are given in Figure S1 with the Cartesian coordinates in Table S2 in the Supporting Information.

For several structures of C_s symmetry, a very small imaginary cage-distorting frequency was calculated with a magnitude of usually less than 10 cm^{-1} . These proved not to be relevant and were ignored.¹⁹ A combination of factors including geometry optimization criteria, SCF convergence, or DFT grid size can contribute to a fictitious imaginary frequency. However, it should be noted that the entropy term is very sensitive to the presence of small vibrational frequencies. Charge analyses were carried out with natural population analysis (NPA) and Wiberg bond index (WBI) at the B3LYP/6-31G(d)/ECP(SDD) level.²⁰

Results and Discussion

In analyzing the catalytic function of CuCl on the cheletropic elimination of 7-PNBD, we focus first on the primary species of this process, that is, the phosphinidene. We therefore start by inspecting (1) the properties of free phosphinidenes and their terminal $W(\text{CO})_5$ complexes, and (2) how these may be formed from the 7-PNBD precursor or isomeric structures. Next, we concentrate on the influence of CuCl by (3) analyzing its complexation to solvents and the various sites of 7-PNBD it can interact with, followed by (4) a detailed study of the decomposition of CuCl-complexed 7-PNBD, and finally (5) the chloride shuttle in the perceived new reactive intermediate and its trapping by olefins. From these analyses, a catalytic cycle is proposed that involves as the key step an S_N2 -like reaction on a CuCl-olefin-complexed $W(\text{CO})_5\text{PR}$. Support for this proposed new intermediate will be provided from an analysis of earlier reported experimental data.

Phosphinidenes. Uncomplexed phosphinidenes (P–R), which resemble nitrenes, will be addressed first, because they enable an evaluation of the applicability of the DFT method employed in this study. Next, we examine the complexed phosphinidenes ($W(\text{CO})_5\text{P}=\text{R}$), which resemble carbenes.

The ground state of NH is a triplet ($^3\Sigma^-$) with the open- ($^1\Delta$) and closed-shell ($^1\Sigma^+$) singlets, respectively, 35.9 and 60.6 kcal/

Table 2. S–T Splitting (kcal/mol) at B3LYP/6-31G(d)+ZPC and Comparison with Experiment and Theory

	open-shell singlet	closed-shell singlet
N–H	35.9 ^a	60.6 ^a
N–Ph	18.5 ^b	33.1, ^c 36.9 ^b
P–H	21.6 ^d	33.4, ^c 28.0 ^e
P–Ph	21.3 ^f	22.9, ^c 25.4, ^f 22.3 ^g

^a Exptl: ref 21. ^b CASPT2(8,8)/6-311G(2d,p)//CASSCF(8,8)/6-31G(d)+ZPC: ref 23. ^c B3LYP/6-31G(d): this work. ^d Exptl: ref 22. ^e QCISD(T)/6-311++G(3df,2p)//MP2/6-31G(d)+ZPC: ref 26a. ^f CASPT2(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d)+ZPC: ref 24. ^g CASPT2(8,8)/ANO//MP2/6-31G(d): ref 26b.

mol higher in energy.²¹ PH also prefers a ground-state triplet $^3\Sigma^-$ (by 21.6 kcal/mol) to the $^1\Delta$ state.²² When a phenyl group replaces the NH hydrogen, the separation between the electronic states of the nitrene is reduced. High-level calculations (CASPT2-(8,8)/6-311G(2d,p)//CASSCF(8,8)/6-31G(d)+ZPC) predict the open-shell and closed-shell singlets of NPh to be, respectively, 18.5 and 36.9 kcal/mol higher in energy than the triplet.²³ For PPh, Borden and co-workers²⁴ obtained S–T energy differences of 21.3 and 25.4 kcal/mol for the open- (1A_2) and closed-shell (1A_1) singlets, respectively, at (CASPT2(8,8)/6-31G(d)//CASSCF(8,8)/6-31G(d)+ZPC).²⁵

Our DFT calculations of the S–T separation for the closed-shell singlet states of PH and PPh (33.4 and 22.9 kcal/mol, respectively) are in good agreement with those performed at high levels of ab initio theory (Table 2).^{24,26} Because the open-shell singlet of both PH and PPh is lower in energy than the closed-shell singlet, we will use in the calculations of reaction energies that involve these species the triplet energy plus the S–T splitting for the open-shell singlet obtained from experiment²² for PH (21.6 kcal/mol) or from calculations²⁴ for PPh (21.3 kcal/mol).

A transition metal (TM) carbonyl group, such as $W(\text{CO})_5$, stabilizes the closed-shell singlet state to the extent that it becomes the ground state.^{27,28} Donation/back-donation to/from the TM carbonyl and from/to the phosphinidene increases the HOMO/LUMO separation, making it analogous to that of carbenes.⁸ For that reason, the reactivity of the $W(\text{CO})_5\text{PR}$ intermediate parallels that of carbenes. However, it should be emphasized that, while the identity of the $W(\text{CO})_5\text{PR}$ species has been inferred, it has not been detected directly by spectroscopic means.

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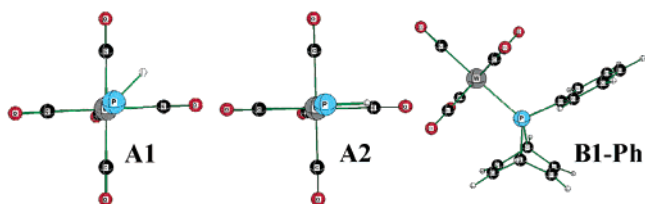


Figure 2. Staggered (**A1**) and eclipsed (**A2**) conformers of $W(CO)_5PH$ and precursor **B1-Ph**.

The phosphinidenes PH and PPh coordinate more strongly to $W(CO)_5$ (56.6 and 60.9 kcal/mol, respectively) than does CO (41.8 and exptl^{29,30} 46.0 kcal/mol).³¹ Both the P–W bond distances in $W(CO)_5PR$ (R = H (**A1**) 2.423, R = Ph (**A1-Ph**) 2.458 Å) and the P–W Wiberg bond indices (WBI) (R = H 1.142, R = Ph 0.934) show more double bond character for the P–W bond of the nonsubstituted phosphinidene complex. The PH staggered (**A1**) and PH eclipsed (**A2**) conformers (Figure 2) of $W(CO)_5PH$ have the same energy. The eclipsed conformer is a transition state, but the zero-point correction cancels the electronic difference. Instead, this rotational barrier is 5.5 kcal/mol for $W(CO)_5PPh$ due to π stabilization, which is reflected in the transition state by its shorter P–W bond (2.428 vs 2.458 Å) and longer P–C bond (1.841 vs 1.814 Å). It might be noted here that the phenyl group is twisted 90° in 7-PNBD (**B1-Ph**) due to the absence of P–Ph conjugation (no empty p-orbital) and the increased steric hindrance around phosphorus.

Phosphinidene Formation. How is $(OC)_5W=PR$ being generated? Direct fragmentation of 7-PNBD (R = H, **B1**) into phosphinidene **A1** and C_6H_6 is presumed to be the most accepted pathway. It has a calculated barrier of 19.3 kcal/mol (**B2**) that is little influenced by the R = Ph substituent (17.9 kcal/mol). The cheletropic elimination occurs in an asynchronous fashion, as illustrated in Figure 3a (R = H).

As an alternative route, we also considered the involvement of 1,2-adducts that can be formed as intermediates via [1,3]-sigmatropic shifts. Recently, Buló et al.³² reported that such a [1,3]- σ shift for $Cr(CO)_5$ -complexed 2-vinylphosphirane into 3-phospholene is 24.7 kcal/mol endothermic and occurs in a pericyclic, but diradical-like, manner ($\Delta H^\ddagger = 46.3$ kcal/mol). The reverse pathway for 7-PNBD would give bicyclic phosphiranes with the $W(CO)_5$ group located either over the benzene ring (“cis” **B3**) or directed away from it (“trans” **B5**) (Figure 3b). Both of these phosphinidene 1,2-adducts are, in fact, more stable than 7-PNBD (8.6 kcal/mol for **B3** and 8.9 kcal/mol for **B5**). However, despite an extensive search, we were unable to locate a transition structure for the [1,3]- σ shift. Following the intrinsic reaction coordinate (IRC) for **B2** leads surprisingly to the slightly less exothermic fragmentation into $W(CO)_5PH$ (**A1**) and C_6H_6 (8.3 kcal/mol). We presume that the transition states for the [1,3]- σ shifts are similar to **B2** and that their possible diradical character³² hampers locating them. The structural

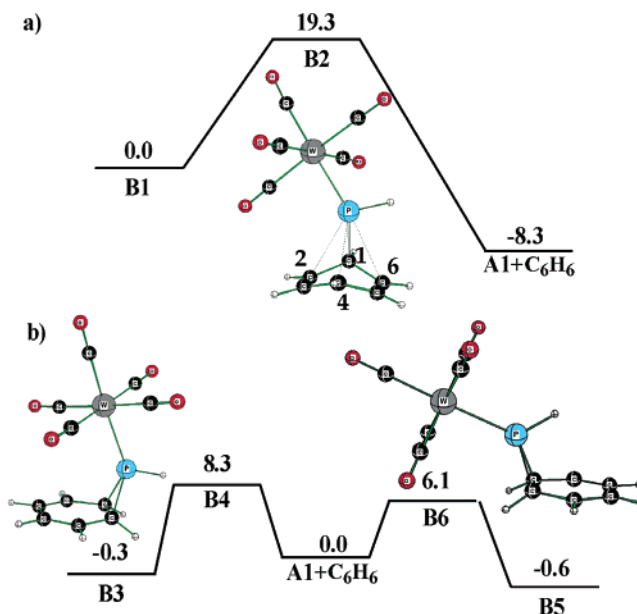


Figure 3. Reaction profile for the decomposition of 7-PNBD (R = H) into $W(CO)_5PH$ and benzene, and the formation of the “cis” (**B3**) and “trans” (**B5**) 1,2-adducts.

properties of **B2** give some support for this proposition. Its breaking P–C₄ bond (2.741 Å) is of length similar to the P–C₆ (2.734 Å) and P–C₂ distances (2.738 Å) that can be associated with forming either the “cis” (**B3**) or the “trans” (**B5**) 1,2-adduct. This would suggest that the 1,3- σ shift also occurs in an asynchronous manner, which is indeed the case for the $Cr(CO)_5$ -complexed vinylphosphiranes.³²

Fragmentation of the 1,2-adducts into $W(CO)_5PH$ and C_6H_6 occurs over low activation barriers, that is, 8.6 kcal/mol for the “cis” form (**B3** → **B4**) and 6.7 kcal/mol for the “trans” form (**B5** → **B6**) (Figure 3). The more favorable entropy will drive the fragmentation into the ultimate products, benzene and the terminal phosphinidene complex.

CuCl Complexes. The influence of copper(I) chloride (CuCl) on the formation and reactions of the phosphinidene complex can be considered to result from the interaction with its precursor but also from those with the olefinic substrate or the aromatic solvent. The latter are discussed first as it simplifies the discussion on the CuCl interaction with 7-PNBD.

Olefin and Solvent Complexes. CuCl forms a donor–acceptor complex with ethylene³³ with a strength of 32.6 kcal/mol. An NBO analysis shows the acceptor $\sigma^*(CuCl)$ orbital to be 94% composed from the 4s orbital of Cu. The energies for the σ^* -(CuCl)– $\pi(C=C)$ and $d_{yz}(CuCl)$ – $\pi^*(C=C)$ interactions amount to 59.6 and 24.1 kcal/mol, respectively, as determined by second-order perturbation theory analysis. There is a net transfer of 0.035 e[−] from CuCl to ethylene.

The complexation energy of CuCl with two ethylenes is only 4.0 kcal/mol more than that for one ethylene as both compete for the same CuCl donor and acceptor orbitals. Thus, the exchange of ethylene is predicted to be facile (eq 1).

CuCl coordinates less tightly to benzene than to ethylene (24.2 vs 32.6 kcal/mol) due to the reduced π donor/acceptor ability of the aromatic molecule. Even a second CuCl can coordinate to $CuCl-C_6H_6$ with almost the same binding energy as the first

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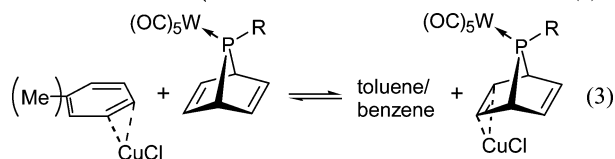
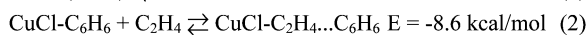
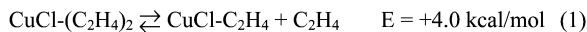
(31) When the closed-shell singlet is taken as reference, the bond energies increase to 68.5 (PH) and 62.6 (PPh) kcal/mol. With respect to this reference, $(OC)_5W=PPh$ has the smaller P–W bond enthalpy because conjugation between the phenyl π orbitals and the empty orbital on phosphorus competes with back-donation from the $W(CO)_5$ fragment.

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(21.5 and 22. kcal/mol in C_{2h} (**C1**) and C_2 (**C2**) symmetry, not shown), but experimentally this is not likely to occur in light of the excess of solvent.

Benzene can be displaced from $\text{CuCl}-\text{C}_6\text{H}_6$ by ethylene, resulting in a weak complex (0.2 kcal/mol) between C_6H_6 and $\text{CuCl}-\text{C}_2\text{H}_4$ (eq 2). This ability of CuCl to weakly coordinate to a second “solvent” molecule will appear to be an important component in the catalytic cycle.



CuCl is expected to dissolve partly in toluene, which is the solvent commonly used in the phosphinidene reactions, by forming a CuCl -toluene complex. We presume the transfer of CuCl from the solvent to 7-PNBD (eq 3) to be similarly exothermic as the CuCl transfer from benzene to ethylene (eq 2). Because of the abundance of solvent molecules, this complexation should be reversible. For part of the potential energy surface, we use ethylene as the solvent rather than toluene or benzene. This should model the essential features of the catalytic cycle except that ethylene coordinates more tightly to CuCl .

7-PNBD Complexes. Four positions were considered for the initial coordination of CuCl to the double bonds of 7-PNBD (endo-syn, endo-anti, exo-syn, and exo-anti, Figure 4), and two positions were considered for coordination to its tungsten (denoted as “W-site1” and “W-site2”, Figure 5). The CuCl binding to these six different positions of 7-PNBD ($R = \text{H}$) varies between 25.3 and 30.8 kcal/mol (Table 3). When a phenyl group is substituted for hydrogen on the phosphorus, the binding energies change very little.

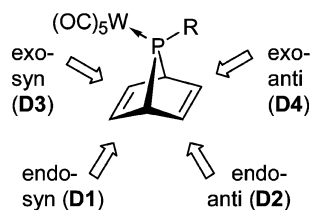


Figure 4.

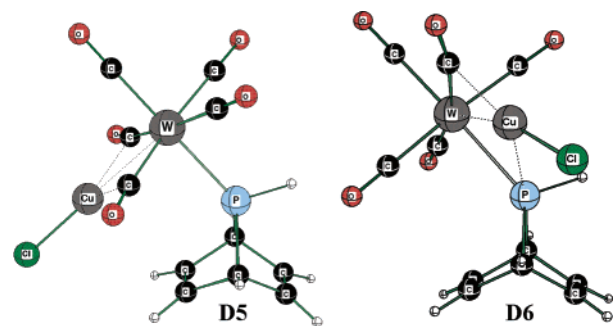


Figure 5. CuCl W1 (left) and W2 (right) sites of 7-PNBD.

Decomposition of CuCl -Complexed 7-PNBD. The barriers for the CuCl -catalyzed fragmentation of 7-PNBD are given in

Table 3. Binding Energies (kcal/mol) of CuCl or $\text{CuCl}-\text{C}_2\text{H}_4$ to 7-PNBD ($R = \text{H}$ and Ph)

	$\text{CuCl}/$ $R = \text{H}$	$\text{CuCl}/$ $R = \text{Ph}$	$\text{CuCl}-\text{C}_2\text{H}_4/$ $R = \text{H}$
endo-syn	-30.3 (D1)	-31.1 ^a (D1-Ph)	
endo-anti	-30.8 (D2)		
exo-syn	-25.3 (D3)		
exo-anti	-29.7 (D4)	-29.9 (D4-Ph)	-1.9 (F1)
W-site1	-25.4 (D5)	-25.4 (D5-Ph)	
W-site2	-26.7 (D6)		4.2 (F2)

^a When CuCl is in the endo-syn binding site, the phenyl group has a 6.9 kcal/mol rotational barrier (**D1-Ph** \rightarrow **D1'-Ph**).

Table 4. Uncatalyzed and Catalyzed Barriers (kcal/mol) for Fragmentation of 7-PNBD ($R = \text{H}$ and Ph)

7-PNBD	ΔE^\ddagger	d_{PC} in TS ^a	ΔE
	$R = \text{H}$		
uncatalyzed	19.3	2.741 (32%)	-8.3
endo-syn (D1 \rightarrow D7)	18.3	2.853 (37%)	-2.5
endo-anti (D2 \rightarrow D8)	19.0	2.883 (38%)	-2.0
exo-syn (D3 \rightarrow D9)	2.7 ^b	<i>c</i>	
exo-anti (D4 \rightarrow D10)	22.5 ^d	1.980 (3%)	
W-site1 (D5 \rightarrow D11)	18.6	2.695 (32%)	-26.9
W-site2 (D6 \rightarrow D12)	12.3	2.450 (27%)	-25.6
	$R = \text{Ph}$		
uncatalyzed	17.9	2.818 (36%)	-13.7
endo-syn (D1-Ph \rightarrow D7-Ph)	17.6	3.043 (43%)	-6.8
exo-anti (D4-Ph \rightarrow D10-Ph)	20.0	2.442 (26%)	<i>e</i>
W-site2 (D6-Ph \rightarrow D12-Ph)	10.9	2.462 (27%)	-32.9

^a PC bond distance at the transition state. The value in parentheses gives the degree (%) of elongation, being $(S - L)/S \times 100$, where S and L are the short and long P-C distances in the transition state. ^b Barrier to the W-site1 complex. ^c Not breaking a P-C bond in the transition state. ^d Barrier to the W-site2 complex. ^e The product of this transition state is not clear. The reaction may form the alternative CuCl binding site, W-site2 (which was not calculated for $R = \text{Ph}$), or may proceed directly to fragments.

Table 4 together with those (entries 1, 8) for the uncatalyzed reactions. They are only modestly affected by the presence of CuCl , except for the W-site2 complex which has a barrier (12.3 kcal/mol) that is significantly less than that for the uncatalyzed fragmentation (19.3 kcal/mol).

The CuCl -induced fragmentation of 7-PNBD has, of course, an overall barrier that is smaller than values given in Table 4, because the energy gained by binding CuCl to 7-PNBD is partly offset by the energy required for liberating CuCl from its solvent complex (e.g., 24.2 kcal/mol for $\text{CuCl}-\text{C}_6\text{H}_6$). However, the essential information is contained in the transition structures for fragmentation, which reflect the rate-determining step, and we will focus on these.

Endo-Olefin Complexes. Having CuCl complexed to the endo site of one of the olefinic bonds of 7-PNBD ($R = \text{H}, \text{Ph}$), in either a syn or an anti fashion, hardly influences the dissociation barrier. The energy needed to expel $\text{W}(\text{CO})_5\text{PR}$ ($R = \text{H}$) changes from 19.3 (uncatalyzed) to 18.3 kcal/mol for the endo-syn CuCl -complex and likewise for $R = \text{Ph}$ from 17.9 to 17.6 kcal/mol (entries 1–3 and 8–9, respectively, in Table 4). CuCl does not complex to both double bonds of 7-PNBD; such a structure represents an endo-syn \rightleftharpoons endo-anti transfer.

Endo complexation reduces the exothermicity for dissociation because the complexation energy of CuCl to the formed benzene is smaller than that for 7-PNBD.

Exo-Olefin Complexes. When CuCl interacts instead with the exo site of one of the double bonds of 7-PNBD, the decomposition follows a different pathway and leads to different products.

From the exo-syn complex (**D3**), a very small activation barrier exists (TS = **D9**, 2.7 kcal/mol) in which CuCl is transferred from the double bond to the transition metal group at W-site1. In this complex (**D5**), copper is not only coordinated to tungsten (Cu–W 2.699 Å), giving a seven-coordinated species, but has mainly strong interactions with two carbonyls (Cu–C 2.204 Å; W–C–O 167.3°).

With CuCl located in the exo-anti quadrant (**D4**), a transition state was located (**D10**) in which a P–C bond is breaking, suggesting an asynchronous elimination of W(CO)₅PH. However, careful analysis revealed it to be the transition state for CuCl migration to W-site2 (**D6**). Complex **D6** has a short distance between copper and one of the carbonyl groups (Cu–C 2.048 Å) and somewhat longer Cu–P and Cu–W distances (2.777 and 2.704 Å). The barrier for the CuCl migration (**D4** → **D10** → **D6**) of 22.5 kcal/mol is much higher than that for the transfer from exo-syn to W-site1, because CuCl becomes nearly dissociated in the migration over the saturated phosphorus group.

Thus, also the exo-olefin complexes do not explain why CuCl influences the cheletropic elimination of 7-PNBD favorably. Instead, they point to the importance of the W-site1 (**D5**) and W-site2 (**D6**) complexes.

Complexes with W(CO)₅. Besides transfer of CuCl from one of the double bonds of 7-PNBD to its transition metal group, such CuCl complexes can also be formed directly. These complexes are, in fact, the key to understanding the catalytic activity.

For W-site1 **D5**, 18.6 kcal/mol (TS = **D11**) is required to cleave a P–C bond (2.695 Å), illustrating an asynchronous dissociation. Whereas the barrier is similar to that for the dissociation of endo CuCl-complex (**D1**), the products of the reaction are different. Besides benzene, W(CO)₅PH–CuCl is formed with CuCl coordinated to the phosphorus lone pair (**E4**, see below). The binding energy of this complex (43.9 kcal/mol) is much larger than the coordination of CuCl to benzene (24.2 kcal/mol), thereby leading to a higher exothermicity for fragmentation than that of the endo CuCl-complexes. Ph substitution further enhances the binding energy for the product complex **E4-Ph** (47.2 kcal/mol).

W-site2 complex **D6** dissociates of all of the CuCl complexes most easily with a barrier of 12.3 kcal/mol. This modest barrier is not only due to the exothermicity for the dissociation but also to the interaction in the transition state (**D12**, Figure 6) of CuCl with the developing phosphinidene, while it assists in breaking a P–C bond (Cu–P 2.202 Å, Cu–C 2.438 Å, P–C 2.445 Å); this view is supported by the Wiberg bond indices (WBI: 0.279 Cu–P, 0.112 Cu–C, 0.505 P–C). From an optimization starting at the **D12** geometry, it was ascertained that CuCl does not insert into the P–C bond to give a metallocycle. One way of looking at the dissociation process is that the P–C σ bond converts into a 3c-2e P–C–Cu bond with the empty copper 4s orbital interacting with the emerging P=W double bond of the terminal phosphinidene (Cu–P–W 76.2°). The NPA charges show an increase in charge on phosphorus with a concurrent decrease on carbon. This electron flow, which opposes the trend expected from the elemental electronegativities, may be due to the ability of the W(CO)₅ group to stabilize extra charge on the phosphorus center.

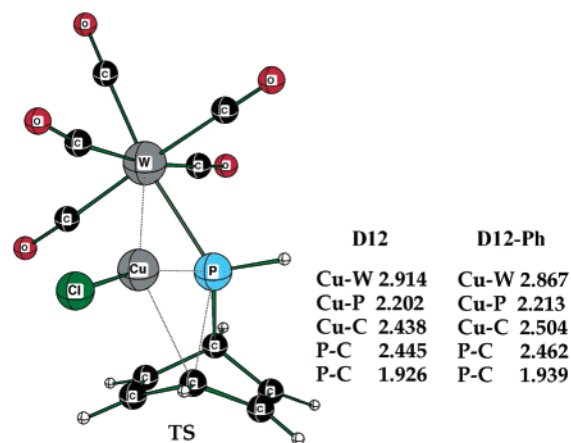


Figure 6. Transition state for the lowest fragmentation barrier of CuCl-complexed 7-PNBD.

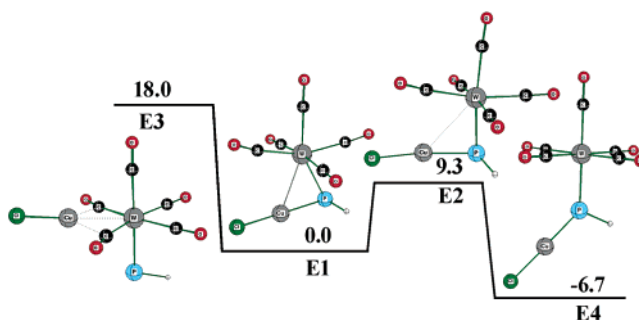


Figure 7. Reaction profile for rearranging π -complexed terminal phosphinidene to the σ -complexed structure.

The initial dissociation product of **D6** is W(CO)₅PH–CuCl complex **E1**. This tight π complex can rearrange (via **E2**, 9.3 kcal/mol) to a 6.7 kcal/mol more stable one (**E4**) where CuCl is coordinated to the phosphorus lone pair (Figure 7). Thus, CuCl coordinates in the initial stage of fragmentation to the P=W π bond of the phosphinidene complex, when the phosphorus lone pair is not yet available, and migrates at a later stage to this lone pair, to give a more stable product. The strength of the CuCl interaction in π complex **E1** can be inferred from the 18.0 kcal/mol barrier for rotating the PH group about the P–W bond (TS = **E3**) and thus out of conjugation with CuCl, which as a result moves into the plane containing tungsten and two carbonyl groups.

The P/C Connection. There is a close parallel between the W(CO)₅PR–CuCl complex and the proposed active catalytic species in the copper-catalyzed cyclopropanations by diazo compounds.^{11,34} In these reactions, a copper(I) complex is thought to coordinate to a diazo carbene to form a metal-complexed carbene. Copper(I) coordinates to the lone pair of the carbene, while the dinitrogen ligand coordinates to the empty p-orbital. As the reaction proceeds, dinitrogen is displaced (solvent-assisted or solvent-unassisted), while the olefin adds either to the copper with subsequent migration or directly to the carbene center. In the corresponding terminal phosphinidene–CuCl complex, the phosphorus center coordinates to the copper(I).

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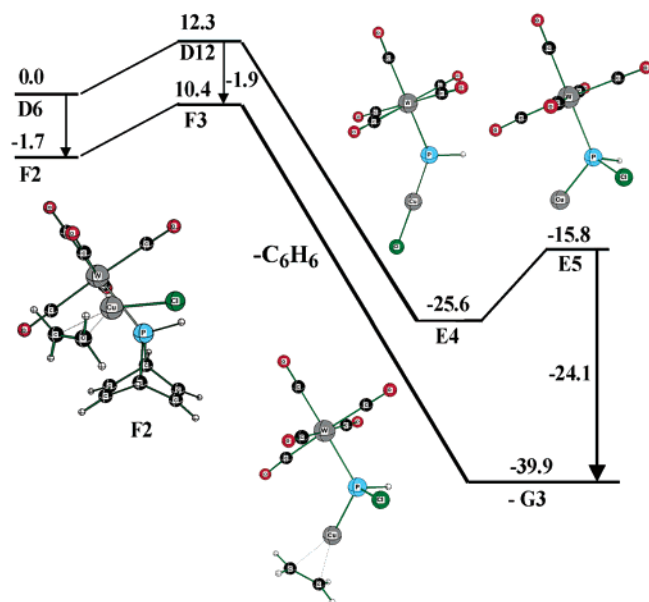


Figure 8. Reaction scheme for the CuCl reaction with 7-PNBD ($R = H$). Complexation with ethylene is exothermic. After benzene is lost, the $W(CO)_5PH(Cl)-Cu-C_2H_4$ complex (**G3**) is formed.

Solvation. There are two reasons to ask whether solvation influences the formation of the phosphinidene from 7-PNBD: (1) will the CuCl-catalyzed fragmentation product, the low-valent $(OC)_5W=P\cdots CuCl$, be stabilized by additional coordination to a solvent molecule, and (2) will the “starting” $CuCl\cdots W$ -site2 complex **D6** be sensitive to solvation in light of the ability of CuCl to interact with, for example, two molecules of ethylene? These issues play, in fact, a prominent role.

To mimic the role of solvent, we explore the effect of ethylene coordination (Figure 8). Addition of ethylene to the copper center of the W-site2 complex **D6** does indeed lead to a small stabilization of 1.7 kcal/mol (**F2**), but because the transition state for fragmentation (**F3**) is influenced likewise (1.9 kcal/mol), there is no net effect on the fragmentation barrier. Instead, the exothermicity of the fragmentation increases by a significant 14.3 kcal/mol, but also leads to a different, Cl-migrated product, $W(CO)_5P(H)Cl-Cu(C_2H_4)$ (**G3**). In the absence of ethylene coordination, this transfer of the chloride ion from copper to phosphorus is endothermic by 9.8 kcal/mol (**E5**). The driving force for the Cl-shift may be attributed to the 24.2 kcal/mol binding energy of ethylene to the copper center in **G3**, which is much more than that in **F2** (1.7 kcal/mol) or in exo-anti isomer **F1** (not shown, 4.8 kcal/mol), but less than that in $CuCl$ -ethylene (32.6 kcal/mol). Thus, ethylene solvation enhances the exothermicity for dissociating 7-PNBD mainly by formation of the modified phosphinidene complex **G3**. The implications are significant.

Phenyl substitution ($R = Ph$) changes the reaction profile slightly because of conjugation with the empty p-orbital on phosphorus, which decreases the driving force for chloride migration. Still, it has a small barrier (albeit 0.3 kcal/mol) for the exothermic Cl-shift (**G1-Ph** \rightarrow **G2-Ph**(TS) \rightarrow **G3-Ph**) (Figure 9). The energy gain of **G3-Ph** with respect to **E4-Ph** is still a considerable 6.5 kcal/mol.

Hence, as surmised from experimental results, the CuCl-catalyzed reaction differs indeed from the uncatalyzed reaction because of the difference in reactive intermediates. Apparently,

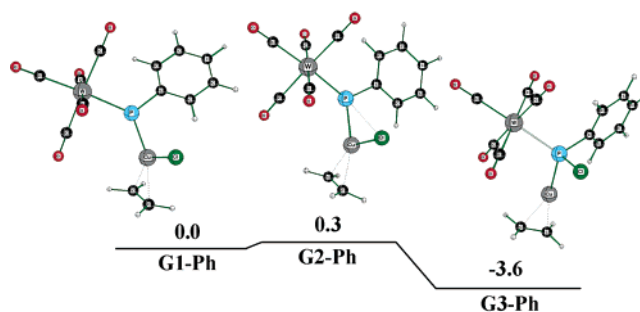


Figure 9. Reaction scheme for the chloride shuttle in **G1-Ph**.

CuCl adds in the catalyzed reaction to the terminal phosphinidene with migration of the chloride to the phosphorus center.

Olefin Trapping. It is well established that when derivatives of 7-PNBD are heated in the presence of an olefin, with or without CuCl, the terminal phosphinidene adds to the double bond to give the complexed three-membered phosphirane.^{6,7} Using ethylene as trapping reagent, we found no barrier for the reaction with $W(CO)_5PH$. This is in accord with experiments that have shown the rates of reactions with various substrates to be dependent solely on the fragmentation of the phosphinidene precursor, that is, first order in 7-PNBD. However, in the olefin addition reaction with $W(CO)_5PH(Cl)-Cu-C_2H_4$ (**G3**), we did locate a transition state (**H1**) with a barrier of 7.8 kcal/mol for formation of the phosphirane (Figure 10). The transition state for this process resembles an S_N2 reaction in that the incoming ethylene displaces the chloride ion back to Cu, which is subsequently expelled as a $CuCl$ -ethylene complex. The reaction is asynchronous as the chloride migration is nearly complete at the transition state. The forming P-C bonds are 2.492 and 2.673 Å, while the P-Cl and Cu-Cl distances are 2.971 and 2.230 Å.

The resulting product complex **H2** is 7.4 kcal/mol more stable than **G3** + C_2H_4 and has Cu-P, Cu-W, and $Cu\cdots C\equiv O$ distances of 2.768, 3.119, and 2.410 Å, respectively. The ultimate products of the reaction, phosphirane complex $W(CO)_5PH-C_2H_4$ (**I1**) and regenerated $CuCl-C_2H_4$, are still 3.6 kcal/mol lower in energy and are separated by an activation barrier (**H2** \rightarrow **H3**) that disappears when zero-point corrections are included. It then appears that the reactive intermediate **G3** and the S_N2 -like addition reaction (**H1**) are the key components of the catalytic cycle in which the $CuCl$ -solvent complex is an active participant.

Catalytic Cycle. The generalized catalytic cycle for the CuCl-catalyzed fragmentation of 7-PNBD and trapping of the reactive intermediate by an olefin is given in Figure 11. In the experimental system, the solvent is generally toluene. For simplicity, our calculations model the solvent-CuCl interactions with ethylene both as solvent and as trapping olefin; as noted, the $CuCl$ -benzene complexation is more modest. The complete reaction profile with relevant structures and relative energies is given in Figure 10.

Of course, the olefin itself, instead of the solvent, may play a supporting role in the CuCl-catalyzed decomposition of 7-PNBD. In such a case, the rate of the reaction will show a dependence on the olefin concentration, but the rate expression is not straightforward due to the competing equilibria rendering the $CuCl$ -benzene and $CuCl$ -olefin complexes.

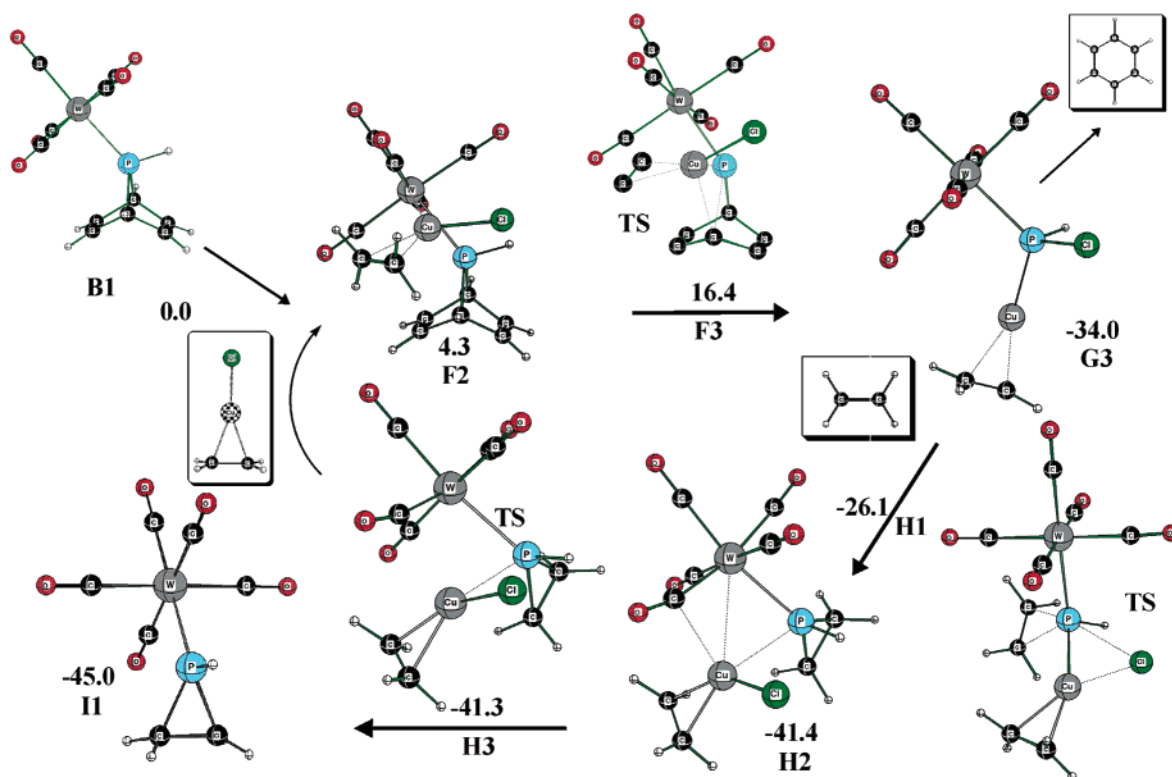


Figure 10. Reaction profile for the catalytic cycle. Energies are given with respect to **B1** and C_2H_4-CuCl .

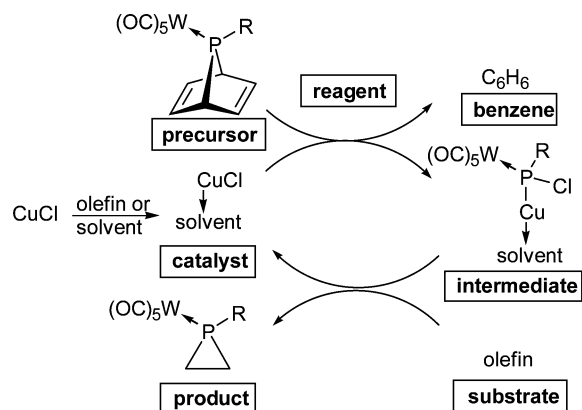


Figure 11. Generalized catalytic cycle for the $CuCl$ -solvent-assisted olefin addition of phosphinidenes.

Taking the solvent complex as the source for $CuCl$, a crude evaluation of the activation parameters can be made for fragmentation of 7-PNBD by taking simplified **D12** as the transition state and ignoring additional solvent or olefin stabilization (Table 5). When $R = H$, the difference between the barrier for the rate-determining step of the uncatalyzed and that of the $CuCl$ -catalyzed reaction is 9.5 kcal/mol, which increases to 10.9 kcal/mol when $R = Ph$. The activation entropy of the catalyzed reaction is more unfavorable than the uncatalyzed reaction, but the difference is only about 12 entropy units because a solvent molecule (benzene) is released at the transition state. At 55 °C, $k_{cat}/k_{uncat} \approx 4 \times 10^4$ for $R = Ph$, which suggests that, even with a low concentration of $CuCl$ -solvent, the catalyzed reaction will be faster.

Supporting Evidence. There is experimental support for the proposed mechanism. The first comes from our study on the $CuCl$ -catalyzed reaction of 7-PNBD with a phospholene (Figure

Table 5. Predicted Activation Parameters, ΔH_a (kcal/mol) and ΔS_a (cal/mol·K), for the Uncatalyzed and $CuCl$ -Catalyzed Decomposition of 7-PNBD ($R = H$ and Ph)

	$R = H$	ΔH_a	ΔS_a
uncatalyzed B1 \rightarrow B2 (TS)		19.3	-1.4
catalyzed $C_6H_6-CuCl + B1 \rightarrow D12$ (TS) + C_6H_6		9.8	-10.0
	$R = Ph$	ΔH_a	ΔS_a
uncatalyzed B1-Ph \rightarrow B2-Ph (TS)		17.9	1.1
catalyzed $C_6H_6-CuCl + B1-Ph \rightarrow D12-Ph$ (TS) + C_6H_6		7.0	-11.0

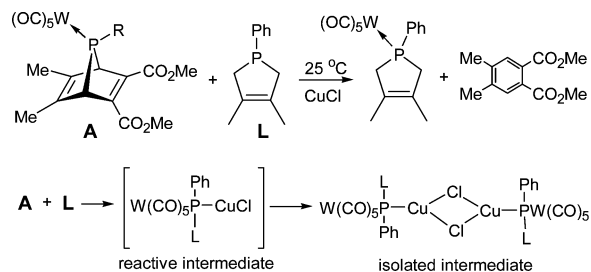


Figure 12. Reaction showing the formation of a $P-Cu_2Cl_2-P$ complex, a dimer of the $CuCl$ -complexed intermediate.

12).¹² With short reaction times and using chloroform as solvent, an intermediate was isolated. The $W(CO)_5$ group in this $P=P$ ylid transfers to the phospholene ligand on longer reaction times. The X-ray structure of the intermediate shows a $CuCl$ dimer with phospholene coordinated to phosphorus as a Lewis base. Apparently, with the weakly coordinating solvent $CHCl_3$, chloride does not migrate, but instead the phospholene coordinates to phosphorus followed by dimerization.

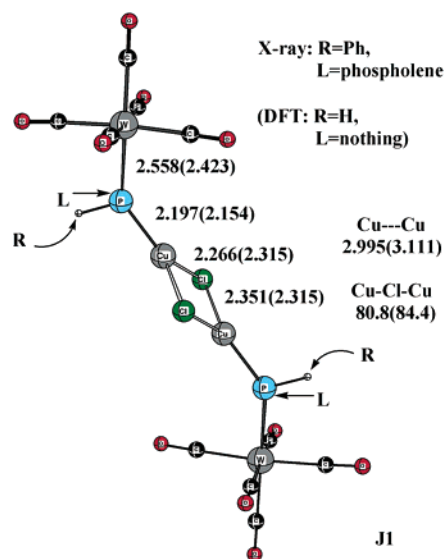


Figure 13. DFT and X-ray structure of **J1**.

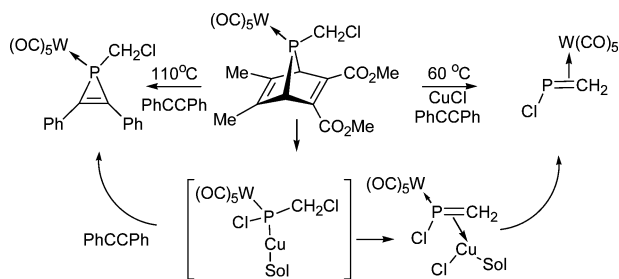


Figure 14. Reactions of a 7-chloromethyl-7-phosphanorbornadiene with an acetylene in the presence and absence of CuCl.

A $W(CO)_5PH-CuCl$ dimer was computed in C_{2h} symmetry,³⁵ which differs from the X-ray structure¹² in that the phospholene ligands are omitted and P-Ph is replaced by P-H (Figure 13).³⁶ The dimerization energy ($2E4 \rightarrow J1$) is 22.0 kcal/mol.³⁷

The second example comes from a study by Deschamps and Mathey,^{3f,g} who found that trapping of the phosphinidene generated from a 7-chloromethyl-7-PNBD derivative with diphenylacetylene gives different products for the CuCl-catalyzed and uncatalyzed reaction. The expected phosphirene was obtained at 110 °C, but at 60 °C and using CuCl a $W(CO)_5$ -stabilized phosphalkene $CIP=CH_2$ results instead where the chlorine has migrated to the phosphorus (Figure 14). The explanation for this observation is now straightforward. The intermediate formed in the CuCl-catalyzed fragmentation of 7-PNBD is $W(CO)_5P(Cl)CH_2Cl-Cu-Sol$, where Sol is the solvent toluene. The CH_2Cl substituent can migrate to the copper center (displacing a solvent molecule) in a reaction that has an 11.5 kcal/mol barrier and is 26.4 kcal/mol exothermic (Figure 14). The complexed CuCl in the resulting phosphalkene

(35) The C_{2h} -symmetry structure has two imaginary frequencies (4i and 13i). Reoptimizing a distorted geometry in C_i symmetry resulted in essentially no change, except for only one imaginary frequency (3i).

(36) While the X-ray structure has close to C_i symmetry, due to the coordinating phospholene ligands, the agreement between theory and the X-ray structure is quite reasonable.

(37) For other examples of a $P-Cu_2Cl_2-P$ core, see: (a) Arnold, P. L. *Heteroat. Chem.* **2002**, *13*, 534. (b) Tulloch, A. A. D.; Danopoulos, A. A.; Kleinhenz, S.; Light, M. E.; Hursthouse, M. B.; Eastham, G. *Organometallics* **2001**, *20*, 2027. (c) Straub, B. F.; Hofmann, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1288. (d) Raubenheimer, H. G.; Cronje, S. *J. Organomet. Chem.* **2001**, *617-618*, 170.

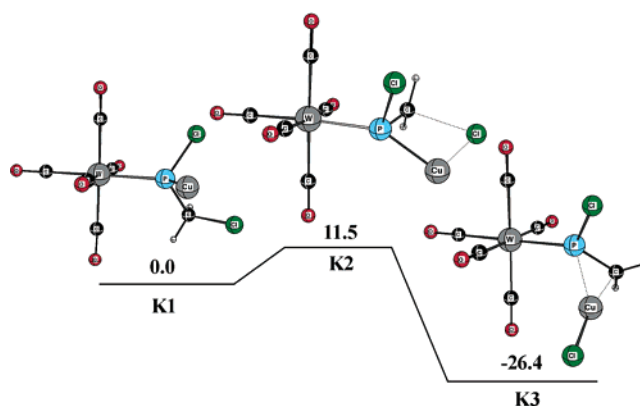


Figure 15. The chloride shuttle in $W(CO)_5P=CH_2Cl-CuCl$.

$W(CO)_5P(Cl)=CH_2-CuCl$ (**K3**) can then easily be expelled by the $W(CO)_5$ group (Figure 15).

Additional support of the proposed mechanism comes from the observed “modest” selectivity in the CuCl-catalyzed reaction of 7-PNBD with various olefins.^{5a} Relative to *cis*-2-butene (1.0), tetramethylene is less reactive (0.2), while isobutylene is more reactive (2–4). These results were not anticipated, because terminal “free” phosphinidene $W(CO)_5PPh$ is expected to show no selectivity,^{3e} and were therefore attributed to entropy factors.^{5a} However, if $W(CO)_5PR(Cl)-Cu-solvent$ is the reactive species, the selectivity may well arise from the chloride “shuttling”-barrier on olefin addition, cf., **G3** + $C_2H_4 \rightarrow H2$, for which the barrier is 7.8 kcal/mol when $R = H$ and the solvent is C_2H_4 . For $R = Ph$, the barrier for olefin trapping is probably smaller, because (1) the $Cu \rightarrow P$ chloride shift (**G1-Ph** \rightarrow **G3-Ph**, ΔE is only 3.6 kcal/mol) has a 0.3 kcal/mol barrier but none for $R = H$, and (2) the olefin interaction with **G1-Ph** is expected to have little or no barrier (Figure 9). Small variations in the “shuttle” barrier would explain the observed olefin selectivity.

Conclusions

The thermal decomposition of 7-PNBD can take place by two mechanisms: uncatalyzed at higher temperatures (110 °C) and CuCl-catalyzed at lower temperatures (55 °C or below). Six different coordination sites have been considered for the CuCl-catalyzed fragmentation of 7-PNBD. The lowest-energy pathway has an activation of 7.0 kcal/mol ($R = Ph$) when the reactants are assumed to be 7-PNBD and the CuCl-benzene complex, which can be compared to a 17.9 kcal/mol ($R = Ph$) barrier for the uncatalyzed reaction. Following the initial fragmentation, the $W(CO)_5PH-CuCl$ complex is predicted to migrate a chloride to phosphorus if a coordinating solvent is available to stabilize the copper ion. The “chloride shuttle” takes place when the trapping reagent displaces the chloride back to copper in an S_N2 -like reaction.

Experimental evidence for the proposed mechanism comes from mainly two sources. First, the X-ray structure of a $P-Cu_2Cl_2-P$ complex, which was an isolable intermediate in a 7-PNBD fragmentation reaction, can be rationalized as the dimer formed by the catalytically active species, $W(CO)_5PR-CuCl$. Second, the trapped product is different depending on whether the reaction is CuCl-catalyzed or not. In the presence of CuCl, the reactive intermediate undergoes a unimolecular rearrangement of the CH_2Cl group to the copper, followed by trapping.

There are obvious parallels between the CuCl-catalyzed fragmentation of 7-PNBD and the copper(I)-catalyzed cyclopropanation reaction. First, both reactions involve a Cu(I) methylene/phosphinidene complex where Cu(I) is coordinated to the lone pair of carbon/phosphorus. Second, a Lewis base (dinitrogen/chloride) is coordinated to the empty p-orbital of carbon/phosphorus that is displaced before (two-step) or during (one-step) the olefin addition to the carbon/phosphorus center.

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Supporting Information Available: The total energies, zero-point energies, molecular plots, and Cartesian coordinates for relevant structures optimized at the B3LYP/6-31(d)/ECP(SDD) level of theory (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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