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Single Electron Transfer-Mediated Selective *endo*- and *exo*cyclic Bond Cleavage Processes in Azaphosphiridine Chromium(0) Complexes: A Computational Study

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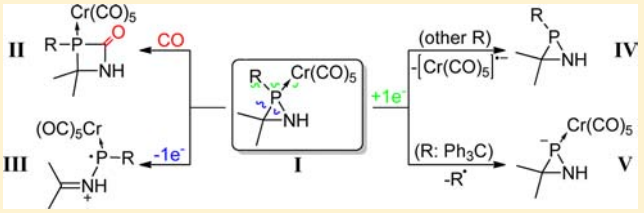
Supporting Information

ABSTRACT: Azaphosphiridines κP pentacarbonylchromium(0) complexes **2a,b** (**2a**: R = H; **2b**: R = Me) exhibit an average ring strain ranging from 24.2 to 25.7 kcal mol^{-1} as obtained from homodesmotic reactions at the LPNO-NCEPA1/def2-TZVPP//BP86/def2-TZVP level. Parent azaphosphiridine chromium complex **1** is more stable than the ylidic *P*-iminiumphosphanide chromium complex isomer **6**, which is obtained from (formal) endocyclic P−C bond cleavage. Computational evidence is provided for an insertion of carbon monoxide into the P−N bond of **1** to form 1,3-azaphosphetidin-2-one chromium complex **11**, as the reaction was exergonic by −15.1 kcal mol^{-1}. The *VBSD* (variation of bond strength descriptors) methodology unveiled that SET (single electron transfer) oxidation of trimethyl-azaphosphiridine chromium complex **2b** results in selective endocyclic P−C bond cleavage to afford the trimethyl-iminiumphosphanyl radical cation complex **13**$^{\bullet+}$. SET reduction of a wide variety of differently *P*-substituted azaphosphiridine complex derivatives (**2a**: R = H; **2b**: R = Me; **2c**: R = Cp; **2d**: R = Cp*; **2e**: R = $CHTms_2$; **2f**: R = CMe_3; **2g**: R = CMe_2Ph; **2h**: R = $CMePh_2$; **2j**: R = Ph; **2k**: R = C_6F_5; Cp*: pentamethylcyclopentadienyl; Tms: trimethylsilyl) lead to selective decomplexation and thus to the corresponding unligated azaphosphiridines **14**. Only in case of the *P*-trityl substituted azaphosphiridine complexes **2i** does the SET reduction preferably cleave the exocyclic P−C bond thus affording azaphosphiridinide complex **12**$^{-}$ and the triphenylmethyl radical.

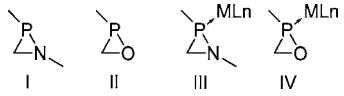


INTRODUCTION

Phosphorus-containing inorganic three-membered heterocycles have attracted broad interest over the years.[1] Despite this fact, the knowledge is still scarce about heterocycles possessing three different polar ring bonds such as in azaphosphiridines[2,3] (**I**) and oxaphosphiranes[4−6] (**II**) (Scheme 1) that have a three-coordinated phosphorus center. This is surprising as there is great potential in their chemistry and/or could have applications as polymer precursors.

Recently, the potential energy surface (PES) of the parent uncoordinated azaphosphiridine **I** was explored[7] and the ring strain of **I** and their *P*-oxides was reported. It was found that *P*-chalcogenides may undergo a ring-expanding rearrangement (RER) to release ring strain with intramolecular $P^{V}\rightarrow P^{III}$ isomerization leading to four-membered 1,3,2-chalcogenaazaphosphetidines. Additionally, *N*-protonation and *N*-complexation of **I** and its *P*-chalcogenides induces selective endocyclic bond cleavage, which was easily estimated by studying the percentage variation of bond strength related descriptors (*VBSD*) of the endocyclic bonds of the precursor and the *N*-protonated or *N*-complexed species. Using pentacarbonylmetal(0) moieties as "inorganic protecting groups" in ligand-centered ring forming reactions provides access to azaphosphiridine[8] **III** and oxaphosphirane[9] complexes **IV** while also preventing ring-dimer formation,[6a] as first observed by Baudler in small-ring phosphorus heterocyclic chemistry.[10] As a result, the chemistry of **III** and **IV** has provided examples of ring enlargement[11] and ring-opening[12] reactions which gives access to larger phosphorus functionalized ring systems. Some challenges which could pave the way for further fundamental experimental studies still remain, such as the development of highly selective methods for exocyclic P−M and P−R bond cleavage while retaining the azaphosphiridine ring structure.

Scheme 1. Three-Membered Phosphorus Heterocycles Containing Another Heteroatom[a]



[a]Lines denote organic substituents, ML_n= $M(CO)_5$, M = Cr, Mo, W.

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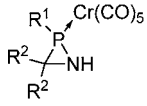
Herein we report on the first systematic theoretical investigation of a wide series of experimentally relevant azaphosphiridine *P*-pentacarbonylchromium(0) complexes **1**−**2** (Scheme 2) with special focus on (i) relative energies of

Scheme 2. Azaphosphiridine Complexes Included in This Study[a]



	R^1	R^2
1	H	H
2a	H	Me
2b	Me	Me
2c	Cp	Me
2d	Cp*	Me
2e	$CHTms_2$	Me
2f	CMe_3	Me
2g	CMe_2Ph	Me
2h	$CMePh_2$	Me
2i	CPh_3	Me
2j	Ph	Me
2k	C_6F_5	Me

[a]Tms: trimethylsilyl; Cp*: pentamethylcyclopentadienyl.

isomers, (ii) ring strain, (iii) ease of exocyclic P−R^1 bond cleavage, (iv) comparative analysis of the *VBSD* methodology as valuable tool for evaluating single electron transfer (SET)-induced bond cleavage processes such as (v) oxidation-induced endocyclic P−C bond cleavage and (vi) reduction-induced selective exocyclic P−R^1 or P−Cr bond cleavage.

COMPUTATIONAL DETAILS

All calculations have been carried out with the ORCA electronic structure program package[13] at a variety of theoretical levels including coupled-cluster theory with single-double and perturbative triple excitations (CCSD(T)), local correlation schemes of type LPNO (Local Pair Natural Orbital) for high level single reference methods such as CEPA (Coupled Electron-Pair Approximation),[14] spin-component scaled second-order Möller-Plesset perturbation theory (SCS-MP2)[15] as well as density functional theory (DFT) calculations using either the BP86[16] or the B3LYP[17] functionals. Grimme's semiempirical correction[18] was included in all B3LYP optimizations and denoted with suffix -D after the functional's name (B3LYP-D). This damped correction accounts for the major part of the contribution of dispersion forces to the energy and was used as implemented by default in the ORCA program: final C6-coefficient scaling factor 1.050, VDW-radii scaling factor 1.100 and damping factor alpha 20.000. For the LPNO-CEPA method, the slightly modified NCEPA/1 version[19] implemented in ORCA was used. For the BP86 and SCS-MP2 methods, the resolution-of-the-identity (RI) approximation[20] was used as well as the new efficient RIJCOSX algorithm[21] in the case of all B3LYP calculations. Ahlrich's triple-ζ valence basis set (TZV) were used together with various sets of polarization functions, either def2-TZVP[22] for geometry optimizations or def2-TZVPP[23] for single-point calculations. Gas-phase geometries were optimized in redundant internal coordinates with tight convergence criteria.[24] Solvent effects (tetrahydrofuran (THF)) were taken into account via the COSMO solvation model[25] where explicitly indicated. Harmonic frequency calculations verified the nature of ground states or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. For the latter, the correct nature of the TSs was checked by intrinsic reaction coordinate (IRC) calculations.

RESULTS AND DISCUSSION

A. Azaphosphiridine $Cr(CO)_5$ Complex Isomers. Following the recent theoretical study on unligated P^{III}-azaphosphiridines (CH_4NP) and their *P*-chalcogenides,[7] we decided to focus on aza-analogues of the most stable isomers of CH_3PO complexes,[26] including dissociation pairs (Figure 1). The reference energy values were computed using CCSD(T)

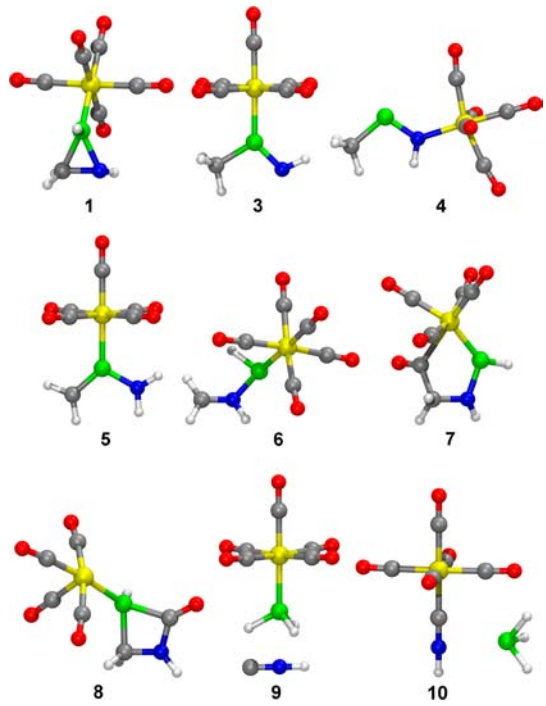


Figure 1. Calculated (SCS-MP2/def2-TZVP) structures for the investigated isomers of $CH_4PNCr(CO)_5$. Arbitrary relative positions in dissociation products **9** and **10**. C, gray; H, white; N, blue; O, red; P, green; Cr, yellow. Drawn with VMD.[27].

together with the flexible enough TZV(2d,2p) basis set. The geometries were obtained at the RI-SCS-MP2/def2-TZVP level (core electrons included in the excitation space), and the harmonic frequencies at this level were employed to compute the zero-point energy (ZPE) correction to the electronic energy (Table 1). Energies obtained with the same SCS-MP2 method using the more polarized def2-TZVPP basis set showed a reasonable agreement.

The quality of the LPNO-NCEPA1 level was confirmed by the obtained results in much better agreement with the high-

Table 1. Relative Energies (kcal mol^{-1}) of the Parent Azaphosphiridine $Cr(CO)_5$ Complex (1) and Its Isomers 3−10 (def2-TZVPP Basis Set)

	SCS-MP2	LPNO-CEPA[a]	CCSD(T)[b]	ZPE[d]
1	23.7	25.8	28.2	61.6
3	3.5	7.4	7.9	61.4
4	0.0	0.0	0.0	42.3
5	5.0	7.1	9.9	60.9
6	35.7	31.0	30.3	61.7
7	67.4	66.2	67.5	67.5
8	56.1	46.2	52.6	52.6
9	37.8	37.4	37.7	54.4
10	30.3	27.5	27.1	53.7
RMSE[c]	3.57	2.55		

[a]Using the NCEPA1 method (see text). [b]TZV(2d,2p) basis set. [c]Relative to those values computed at the CCSD(T) level (in kcal mol^{-1}). [d]ZPE calculated using the optimization level (SCS-MP2/def2-TZVP).

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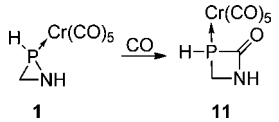
level CCSD(T) energies, according to the low RMSE (root mean square error) value, than SCS-MP2 with the same basis set.

At the highest level, the most stable isomers are the κ*N*- and κ*P*-coordinated iminophosphanes **4** and **3**, respectively, with **4** being slightly favored. It is worth mentioning that for the case of the related study on isomers of the oxaphosphirane complex, the **4**-analogous κ*O*-coordinated phosphinidene oxide was not found as a minimum, but instead a side-on complex (+12.8 kcalmol^{-1}) that corresponded to the phosphinidene oxide κ*P*-complex.[26] The *P*-aminophosphaalkene κ*P*-complex **5** was also found to be of comparable stability. In relation to these three stable isomers, the azaphosphiridine complex **1** is around 20 kcal mol^{-1} less stable, but significantly favored over the endocyclic P−C bond cleavage product **6** which was found to be 9.3 kcal mol^{-1} less stable (than **1**) at the highest level of theory. This may be already taken as indication that the *P*-coordinated ring system is reasonably stable toward ring cleavage in its ground state.

Complexes **7** and **8** formally represent high energy products from RER processes: In the first case, a formal P−C bond cleavage in azaphosphiridine complex **1** and reaction of the C terminus with a carbonyl ligand C atom ([1,3]C P→C shift) would give rise to **7**. In the second case, formal P−N bond cleavage in complex **1** and reaction of the N terminus with a carbonyl ligand C atom ([1,3]N P→C shift) would furnish a five-membered chromacycle. Such species constitutes a minimum on the B3LYP-D PES but not at the SCS-MP2 level and may rearrange via an acyl [1,2] Cr→P shift to complex **8**. As **8** possesses a coordinatively unsaturated chromium center it could easily take up a carbonyl unit (if provided) to yield 1,3-azaphosphetidin-2-one complex **11** as a potential product. This could represent a viable target for further experiments. Therefore, the CO-promoted P−N insertion reaction was studied (Scheme 3) and an overall

Scheme 3. Carbonyl Insertion into the P−N Bond of 1

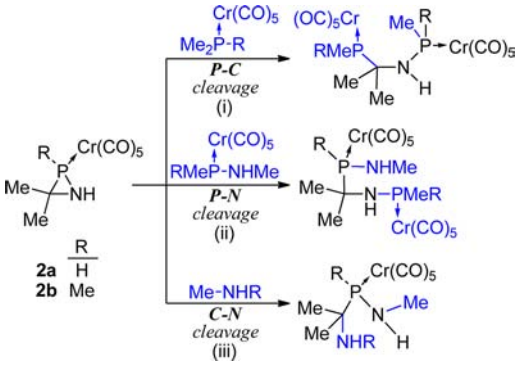


1 **11**

(ZPE corrected) energy of −14.6 kcal mol^{-1} was computed at the highest CCSD(T)/TZV(2d,2p)//SCS-MP2/def2-TZVP level (−15.1 kcal mol^{-1} with LNPO-NCEPA1/def2-TZVPP//SCS-MP2/def2-TZVP). A good estimation of −13.8 kcal mol^{-1} was obtained at the computationally much more inexpensive B3LYP-D/def2-TZVPP//B3LYP-D/def2-TZVP level.

B. Ring Strain of *P*-Complexed Azaphosphiridines. A characteristic feature of small rings systems is the enhanced amount of strain,[28] which generally guides their reactivity. It is therefore important to computationally study these species, in this case azaphosphiridines, to predict how small rings bearing a phosphorus atom compare to other known ring systems. Its quantitative evaluation has been performed by using appropriate homodesmotic reactions, similar to those in the case of uncoordinated and P^{V}-azaphosphiridine derivatives (Scheme 4),[7] in which the number and type of bonds and the valencies of all atoms are conserved.[29] The ring strain is then obtained by changing the sign of the reaction energy. The energy values were computed by single point (SP) calculations at the LPNO-NCEPA1 and SCS-MP2 levels, using the def2-TZVPP basis set

Scheme 4. Homodesmotic Reactions i−iii for the Ring-Opening of Azaphosphiridine Cr(CO)$_5$ Complexes



and the geometries and ZPE correction obtained at the BP86/def2-TZVP level of theory. To enable comparison with previously reported values in *P*-uncomplexed systems, only the 2,3,3-trimethyl-substituted derivative **2b**, as well as the simpler **2a**, were chosen for this study.

The energetics for the homodesmotic ROR in two of the simplest cases **2a−b** are summarized in Table 2. Inspection of

Table 2. Ring Strain (kcal mol^{-1}) from Homodesmotic Reactions of PC-, PN-, and CN-Bond Cleavage,[a] Geometry Optimization, and ZPE Calculation Using BP86/def2-TZVP

		SCS-MP2	LPNO-NCEPA/1
2a	PC	19.5	21.9
	PN	25.9 (24.1)	27.5 (25.7)
	CN	27.0	27.6
2b	PC	19.3	21.8
	PN	22.7 (22.9)	24.3 (24.2)
	CN	26.6	26.5

[a]Using def2-TZVPP basis set; mean values in parentheses.

the data revealed that for the trimethyl substituted system **2b**, the average ring strain at the SCS-MP2 level remains essentially unchanged in relation to that reported (22.6 kcal mol^{-1}) for the uncomplexed system with energies computed at the same level on geometries obtained at the BP86/def2-TZVP level.[7]

C. Bond Cleavage of the Exocyclic P−R Bond. New interesting features of azaphosphiridine *P*-complexes may result from the type of functional groups bonded to the P atom. Through appropriate tuning of the electronic properties and steric bulk of the *P*-substituent, exocyclic P−R bond cleavage may be achieved via release of steric repulsion, and favored when stable fragments are formed. The three fundamental cleavage pathways *A*-*C* are displayed in Scheme 5 leading to the corresponding anionic (**12**$^{-}$), radical (**12**·) and cationic (**12**$^{+}$) azaphosphiridine complex derivatives.

The computed energies for all three processes *A*-*C* are collected in Table 3. As ionic species are involved, solvent effects should be of particular importance and thus they were taken into account using the COSMO model for THF.

On inspection of Table 3 it immediately becomes apparent that the least favored cleavage path is represented by the heterolytic cleavage path *C* leading to the intrinsically unstable cationic species **12**$^{+}$. The different positive values reflect the relative ability of the substituent R to accommodate a negative charge and, therefore, the lowest values correspond to cyclopentadienyl (**2c−d**) and trityl (**2i**) groups, the latter

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Scheme 5. Fundamental bond cleavage processes *A*-*C* of the P−R bond

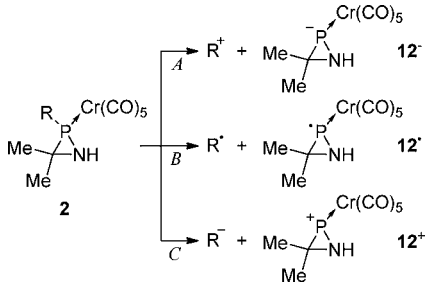

Table 3. Computed ($COSMO_{THF}$/B3LYP-D/def2-TZVP) Energetics[a] (kcal mol^{-1}) for the Dissociation and Redox Processes of Compounds 2b−k, According to Schemes 5, 6, and 7

	$R^+/12^-$	$R^•/12^•$	$R^-/12^+$	$2^{•+}$ [b]	14[c]
2b	111.5	64.9	130.0	7.4	−2.8
2c	72.8	38.0	69.1	7.7	−5.4
2d	31.4	25.4	75.2	2.0	−9.4
2e	36.6	48.6	98.2	5.8	−5.6
2f	33.3	43.2	120.8	6.4	−8.1
2g	24.2	30.5	93.0	6.1	−9.3
2h	17.0	24.4	79.1	6.4	−9.4
2i	−1.9	6.7	58.1	5.8	−18.3
2j	98.6	72.4	118.7	6.6	−5.6
2k	142.5	76.2	81.7	10.4	−7.3

[a]ZPE correction (in kcal mol^{-1}) at the same level. [b]Using $FcH^{•+}$ computed at the same level as oxidant. [c]Reductive cleavage with elimination of $[Cr(CO)_5]^{•-}$ using bis(diglyme)sodium naphthalenide, computed at the same level, as reducing agent.

promoting an additional steric release as previously indicated. The homolytic bond dissociation (path *B*) is more favored and leads to the (essentially) phosphorus-centered radical **12**• (Mulliken spin density: P 0.607, Cr, 0.267, N 0.114 au) and the radical corresponding to the *P*-substituent, R•. The R group is again responsible for the lower dissociation values found for **2d**, **2h** and especially **2i** which goes in line with the increasing radical stability. Finally, in most cases the opposite heterolytic bond cleavage (path *A*) is the most favored, owing to the relative high stability of the heterocyclic fragment 12^- bearing a negative charge at phosphorus (= azaphosphiridinide). Moreover, bulky substituents able to stabilize a positive charge, such as those attached through a tertiary carbon atom (as in **2d** and **2f**−**i**), display rather low dissociation energies. In the limiting case of **2i** bearing the bulky trityl group that forms a stable carbocation, the heterolytic P−R bond dissociation following path *A* was found to be an exergonic process. This in silico finding may turn out to be of great practical relevance as the preparation of *P*-trityl substituted azaphosphiridines is currently being investigated and, hence, anionic derivatives of type 12^- may be used in situ.

D. Bond Activation through SET Oxidation. The idea that different parts of the azaphosphiridine complex could be stabilized or activated toward bond splitting through gain or loss of electron density brought us to the possibility of effecting selective bond activation by SET processes.[30]

According to the simple yet effective *VBSD* methodology that was recently established[7] it is possible to get first insight into the reactivity promoted by any "chemical perturbation" through evaluating the change of the bond strength parameters in comparison to the unperturbed system. In the current study the "perturbation" consists of either removing one electron on the frozen geometry of the neutral (denoted as [0]) compound **2b**, to yield the geometrically frozen radical-cation "[0]+1" or adding one electron, thus affording the geometrically frozen radical-anion species "[0]-1". The percentage *VBSD* on every endocyclic bond, as well as on the exocyclic P−Cr bond, in relation to the parameters featured by the unperturbed compound **2b**, are displayed in Figure 2. Among several

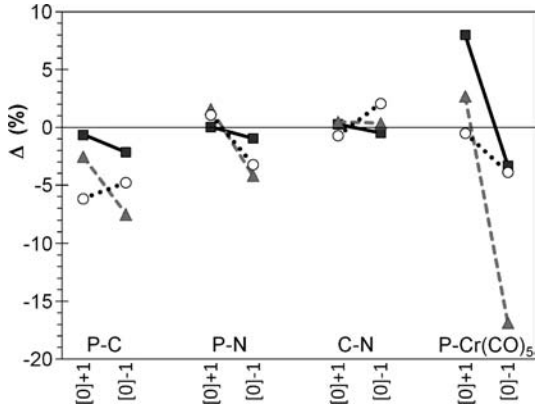

Figure 2. Percentage *VBSD* for endocyclic and P−Cr bonds (B3LYP-D/def2-TZVPP) upon one-electron oxidation ([0]+1) or reduction ([0]-1) with the frozen geometry of (neutral) compound **2b** (B3LYP-D/def2-TZVP): $\rho(\mathbf{r}_c)$ (black solid lines and squares), WBI (gray dashed lines and triangles), and MBO (gray dotted lines and circles).

possible bond-strength related descriptors, we have chosen the electron density at bond critical points, $\rho(\mathbf{r}_c)$, which was successfully used in quantifying many other different bonding situations[31] and is derived from Bader's atoms-in-molecules (AIM) theory.[32] On the other hand, we turned to two of the so-called "bond order" quantities, among which we selected the widespread used[33] Wiberg's bond index (WBI)[34] resulting from the Natural Bond Orbital (NBO) analysis and Mayer's bond order (MBO).[35]

Figure 2 reveals that, apart from some strengthening of the exocyclic P−Cr bond, oxidation ([0]+1) of **2b** has no effect on the P−N and C−N bonds, but seems to weaken significantly the P−C bond. Furthermore, it may be deducible from the highest occupied molecular orbital (HOMO) of **2b** (Figure 3), which has a larger endocyclic bonding contribution between P (green) and C (gray), that the P−C bond may be especially weakened upon oxidation. It is also worth noting that the C−N interaction in the HOMO is basically of π^*-type.

When the geometrically frozen radical-cation ([0]+1) is allowed to relax to a minimum energy structure, the true radical-cation species $2^{•+}$ (i.e., the corresponding "[+1]+1" species) is formed (Scheme 6) featuring an elongated and weakened P−C bond (for $\mathbf{2b}^{•+}$: d_{P-C} = 1.850 Å; $\rho(\mathbf{r}_c)_{P-C}$ =14.85 × $10^{-2}e\ a_0^{-3}$; WBI_{P-C} = 0.843; MBO_{P-C} = 0.916).[37] Table 3 collects the energetics for the oxidation of **2** to $2^{•+}$ by the action of ferrocenium cation (i.e., corresponding to the reaction $2 + FcH^{•+} \rightarrow 2^{•+} + FcH$). At the working level of theory and the chosen oxidation conditions all processes were moderately endergonic, most of them in a narrow range close to 6 kcal mol^{-1}. As expected, the azaphosphiridine complex bearing the strong electron withdrawing pentafluorophenyl group, **2k**, was the most difficult to oxidize within this series,

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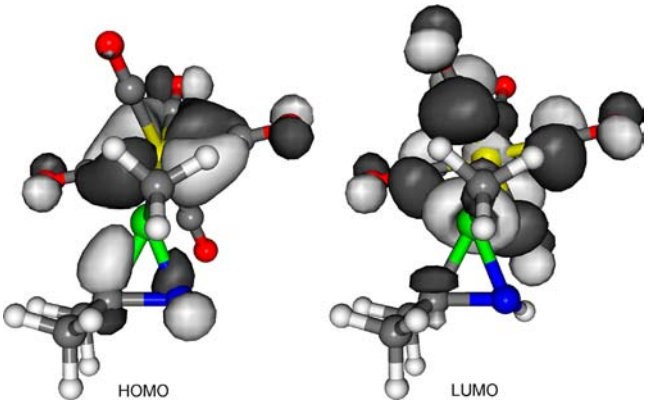
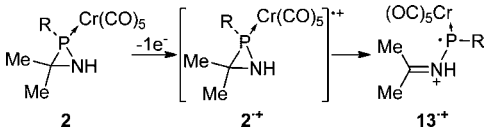


Figure 3. Calculated (B3LYP-D/def2-TZVP) Kohn–Sham isosurfaces (0.04 isovalue) for the HOMO (left) and LUMO (right) of trimethylazaphosphiridine complex **2b**. C, gray; H, white; N, blue; O, red; P, green; Cr, yellow. Drawn with Molekel.[36].

Scheme 6. Oxidation-Directed Endocyclic P–C Bond Cleavage

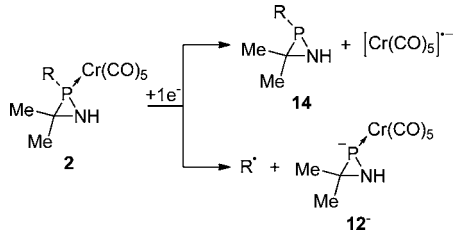


whereas the *P*-pentamethylcyclopentadienyl-substituted derivative **2d** displayed the greatest ease for oxidation. For the sake of simplicity the trimethyl-substituted derivative **2b**$^{\bullet+}$ was selected for studying the full path of P–C bond cleavage at the $COSMO_{THF}$/B3LYP-D/def2-TZVP level. Thus, starting from **2b**$^{\bullet+}$ the P–C bond cleavage product **13b**$^{\bullet+}$ (Scheme 6) was found to be exergonic enough (ΔE = −21.2 kcal mol^{-1}) to enable for the compensation of the first endergonic oxidation step (**2b** → **2b**$^{\bullet+}$) by the action of the ferrocenium ion (Table 3), and proceeds through a low lying transition state (ΔE^{TS} = 6.4 kcal mol^{-1}) whose structure very much resembles that of the ground state **2b**$^{\bullet+}$ itself (see the Supporting Information).

E. Bond Activation through SET Reduction. The alternative SET activation that could be easily envisioned for the azaphosphiridine complexes **2** comes via reduction to give radical anions. Such processes would partially fill the lowest unoccupied molecular orbital (LUMO; Figure 3) having a net antibonding character with respect to the P–Cr interaction. This fact also becomes apparent upon inspection of Figure 2, in which the most pronounced bonding effect on the geometrically frozen radical-anion ([0]-1) species is the remarkable weakening of the exocyclic P–Cr bond, together with some minor weakening of the endocyclic P–C and P–N bonds.

To check the above-mentioned observations, the frozen ([0]-1) geometry was allowed to relax to a minimum energy structure. Upon optimization, the P–Cr bond dissociated and the unstable radical anion structure split into the uncomplexed azaphosphiridine **14b** and the radical anion species [Cr(CO)$_5$]$^{\bullet-}$ (Scheme 7). For saving computational resources and time, every geometrical relaxation process was followed until a bond elongation threshold value of 3.8 Å was reached, from which the bond was considered as cleaved. The energetics for all complexes **2b–k** were computed using the bis(diglyme)-sodium naphthalenide complex[38] as reducing agent (Table 3). Under these conditions all reductive decomplexation processes were exergonic and afforded the decomplexation product

Scheme 7. Reduction-Mediated Exocyclic Bond Cleavages



following a barrierless process from the activated radical anion "**2**$^{\bullet-}$". The exception, having the largest overall exergonic balance, was **2i**. All other cases represent a promising approach for the decomplexation of azaphosphiridine (and possibly other small ring *P*-containing heterocyclic ligands) that up to now are seriously resistant to undergo decomplexation using typical experimental procedures and conditions.

In the particular case of the *P*-trityl substituted azaphosphiridine complex **2i**, in which the P–Cr bond dissociation seems to be possible partially because of the large energy contribution of the steric release around the P atom, the alternative cleavage of the exocyclic P–R bond was much more favorable (ΔE = −31.1 kcal mol^{-1} at $COSMO_{THF}$/B3LYP-D/def2-TZVP). This occurs in a barrierless process to afford the stable trityl radical and the complexed azaphosphiridinide anion **12**$^-$ (Scheme 7). Large steric crowding imposed by the trityl substituent that dramatically enlarges and weakens the exocyclic P–C bond (1.828, 1.911, 1.915, 1.938, and 1.997 Å for **2b**, **2e**, **2g**, **2h**, and **2i**, respectively), as well as the unusually high stability of the trityl radical compared to other typical radicals R, results in the very different behavior of **2i**. This alternative route may be effective to gain access to interesting species such as **12**$^-$ as new building blocks for further functionalization.

■ CONCLUSIONS

This computational study provides first insights into the stability of the azaphosphiridine *P*-pentacarbonylchromium(0) complexes **1–2** by inspecting the PES of the parent compound **1** and a broad set of derivatives **2**. It appeared that **1** possesses higher stability compared to ring-opened isomers such as **6** (by 9.3 kcal mol^{-1}). The isomeric complex **8**, having only a five-coordinate chromium center, led to the idea that carbonyl insertion into the P–N bond may be a favored follow-up reaction yielding 1,3-azaphosphetidin-2-one complex **11**, provided that carbon monoxide is additionally available. Neutral complexes **2** exhibited moderate ring strain (ca. 25 kcal mol^{-1}) similar to the free ligands and thus revealed little effect of *P*-ligation to pentacarbonylchromium. The simple to use *VBSD* (variation of bond strength descriptors) methodology unveiled (in a facile and fast manner) that SET oxidation selectively promotes endocyclic P–C bond cleavage complex **13**$^{\bullet+}$ and SET reduction selectively effect decomplexation and, hence, may pave a way to access hitherto unknown and synthetically promising free ligands **14**. Exclusively in the case of the *P*-trityl substituted azaphosphiridine complex **2i**, the one-electron reduction addressed the exocyclic P–C bond and, hence, afforded the azaphosphiridinide complex **12**$^-$ and the trityl radical.

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■ ASSOCIATED CONTENT

Supporting Information

Bond strength related descriptors for **2b** and the geometrically frozen one-electron oxidized and reduced species. Calculated structures and energies for all species involved in the P−C cleavage reaction of $\mathbf{2b}^{\bullet+}$. Computed structure for the 1,3-azaphosphetidin-2-one **11** and bis(diglyme)sodium naphthalenide complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Anthony J. Arduengo III on the occasion of his 60th birthday.

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