Ab Initio MO Study on Cationic Phosphenium Complexes of Group 6 Transition Metals, *fac*- and *mer*-[(bpy)(CO)$_3$M{$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me}]$^+$ (M = Mo, W)

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Quantum mechanical ab initio calculations at the RHF level of theory using effective core potentials (ECP) for the metals and several all-electron basis sets are reported for the facial and meridional isomers of cationic phosphenium complexes of group 6 transition metals, [(bpy)(CO)$_3$M{$\overline{\mathrm{PN(Me)CH_2CH_2N}}$Me}]$^+$ (M = Mo,W). Fully optimized geometries using the ECP by Stevens et al. are in good agreement with the experimental parameters for the related complex. The theoretically predicted relative thermodynamic stability of the meridional and facial isomers of Mo and W complexes also agrees well with experimental behavior. Structural consideration, M−P(phosphenium) bond rotational behavior, and Mulliken charge and orbital population analysis of component atoms in the central part based on the computational results reveal that (i) a phosphenium ligand has strong π-electron accepting character, which is stronger than that of a CO ligand, and (ii) a phosphenium ligand gets π-donation predominantly from a transition metal and little from amino groups being substituents on the phosphenium phosphorus, though a metal-free phosphenium has such π-donation from N to P. Energy profiles in terms of phosphenium rotation along the M−P bond is also discussed.

Introduction

Interest in a cationic phosphenium species described as [PR$_2$]$^+$ is derived, in part, from the presence of lone pair electrons and a vacant p orbital on the phosphorus atom.[1] A cationic phosphenium ion can be considered to be analogous to carbene and its higher homologues (silylene, germylene, and stannylene), except for a higher cationic charge accumulation on the phosphorus atom. Therefore, its transition metal chemistry as well as its own chemistry has attracted considerable attention. Since the first report of Parry and co-workers in 1978,[2] research efforts have been devoted to the development of transition metal complexes containing a phosphenium species as a ligand.[3−8]

We recently reported a new method for the preparation of cationic phosphenium complexes of group 6

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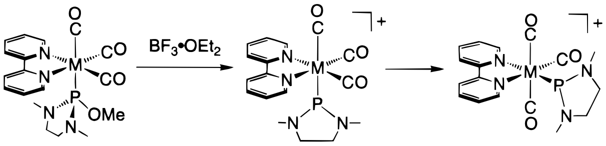
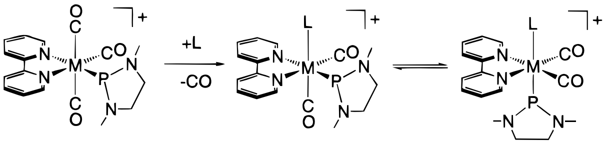
transition metals and their reactivities (see eqs 1 and 2).[6a−d] The starting complex, *fac*-[(bpy)(CO)$_3$M{PNN(OR)}], has one 2,2′-bipyridine (bpy), three CO's, and one diamino-substituted phosphite, PNN(OR) (PNN stands for a $\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}$ fragment in this paper) in a facial form. When the complex reacts with a Lewis acid such as BF$_3$·OEt$_2$ or BCl$_3$, an OR group on the coordinated phosphite is extracted as an anion to give a cationic phosphenium complex keeping its facial geometry. The phosphenium complex then isomerizes to the meridional form (eq 1). Equation 2 shows that the meridional phosphenium complex thus formed reacts with a phosphite (L) to give *cis*-[(bpy)(CO)$_2$ML{PNN}]$^+$ by a CO/L substitution reaction. The cis phosphenium complex isomerizes to its trans form, eventually reaching a cis−trans equilibrium.[6d]



(1)



(2)

The fac−mer isomerization and the CO/L substitution of a cationic phosphenium complex [(bpy)(CO)$_3$M{PNN}]$^+$ can reasonably be explained in terms of a strong affinity of phosphenium ligands for π electrons from filled d orbitals of transition metals. Namely, (i) the phosphenium ligand can accept more π-back-donation in the mer isomer than in the fac isomer, because the phosphenium ligand is trans to bpy in the mer isomer, while in the fac isomer it is trans to the CO ligand, which also requires strong π-back-donation, (ii) the strong π-acceptability of the phosphenium reduces π-back-donation from the transition metal to the CO ligands, causing a labilization of these CO ligands. Further support for the strong π-acceptability of a phosphenium ligand can be seen in the X-ray-determined structures of the Mo complexes, *trans*-[(bpy)(CO)$_2$LMo{PNN}]$^+$, showing that an Mo−P(phosphenium) bond has considerable double-bond character.[6d]

Theoretical treatments of phosphenium cations have been undertaken.[1] However, calculations on phosphenium complexes in which the transition metal possesses a full coordination sphere have not been reported to date.[8a] Considering the importance of cationic phosphenium complexes, it seems worthwhile to subject the phosphenium complexes described in eq 1 to an ab initio MO study. In this study, we report the nature of an M−P(phosphenium) bond from a theoretical point of view, relative energies among their isomers, and rotational energy barriers along the M−P bond.

Computational Details

The geometric parameters of the facial and meridional forms of phosphenium complexes, [(bpy)(CO)$_3$M{PNN}]$^+$ (M = Mo, W), were optimized by the energy gradient method at the ab initio RHF level of theory. In addtion to the standard contracted Gaussian basis sets, effective core potentials (ECPs) were used to replace the chemically less important core orbitals to make the calculations feasible for transition metals. Basis sets and ECPs used for full geometry optimizations are as follows: ECPs with the valence double-ζ basis sets of Stevens, Krauss, Basch, and Jasien (SKBJ),[9] another ECPs LANL2MB with valence basis sets of single-ζ quality by Hay and Wadt,[10] and the standard minimal basis set, STO-3G, by Pople and co-workers.[11] The first ones were augmented with a set of d-polarization functions with standard exponents such as 0.55 for P and 0.80 for C, N, and O,[12] which is denoted as SKBJ(d) in this paper. The other ECPs LANL2DZ with valence basis sets of double-ζ quality by Hay and Wadt[10] and 3-21G* with polarization functions by the Pople group[13] were used for single-point energy calculations and optimizations of the limited geometric parameters related to the six ligands directly interacting with the central metal. Single-point energy calculations using density functional theory (DFT) were also carried out. As for the DFT level of theory, Becke's three-parameter gradient-corrected exchange functional was applied along with the gradient-corrected correlation functional of Lee, Young, and Parr (B3LYP).[14]

All the calculations reported in this paper were performed using the ab initio quantum chemistry program packages GAMESS[15] and GAUSSIAN98.[16]

Results and Discussion

Relative Energies and Geometric Features of *fac*(0) and *mer*(90) for the Mo Complex. The geometric parameters of facial or meridional phosphenium complexes in eq 1 have not been reported experimentally. Therefore, the first step of this study is to obtain these parameters reliably. Two X-ray structures of Mo phosphenium complexes related to those in eq 1 have been reported: *trans*-[(bpy)(CO)$_2$Mo{$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}$(OMe)}{$\overline{\mathrm{PN(Me)CH_2CH_2N}}\mathrm{Me}$}] (OSO$_2CF_3$) (**1**) and *trans*-[(phen)(CO)$_2$Mo{$\overline{\mathrm{PN(^tBu)CH_2CH_2O}}$(OMe)}{$\overline{\mathrm{PN(^tBu)CH_2}}$-

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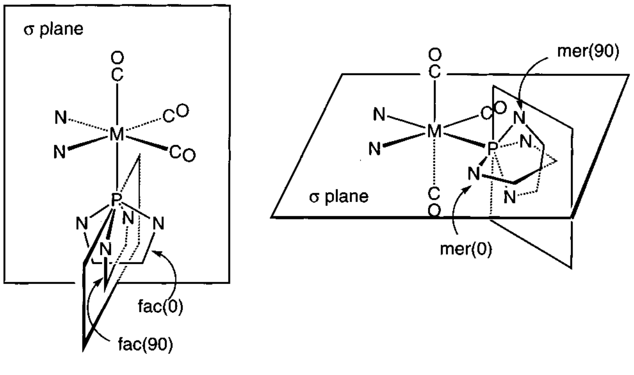
Table 1. Selected Fully Optimized Geometric Parameters of *fac*(0)-[(bpy)(CO)$_3$Mo{PNN}]$^+$ and X-ray Determined Parameters of *trans*-[(bpy)(CO)$_2$Mo{PN(Me)CH$_2$CH$_2$NMe(OMe)}{PNN}]$^+$ (1)

	basis sets			
	STO-3G	LANL2MB	SKBJ(d)	exptl[6d]
		Bond Distances in Å		
Mo−P	2.177	2.407	2.277	2.254(1)
Mo−N	2.235	2.267	2.350	2.244(4), 2.255(4)
Mo−C[a]	1.921	2.133	2.050	1.953(6), 1.966(6)
C−O[a]	1.165	1.151	1.139	1.158(7), 1.148(7)
P−N[b]	1.705, 1.708	1.759, 1.756	1.637, 1.640	1.642(5), 1.644(5)
N−C (in Me)[b]	1.464, 1.461	1.461, 1.462	1.472, 1.468	1.46(1), 1.43(1)
N−C (in CH$_2$)[b]	1.470, 1.470	1.470, 1.471	1.471, 1.470	1.453(8), 1.449(8)
		Angles in deg		
Mo−P−N	132.7, 135.2	133.4, 135.7	131.8, 134.4	132.7
N−P−N[b]	92.1	91.0	93.8	92.6
P−N−C (in Me)[b]	124.8, 124.7	123.9, 123.8	125.5, 124.7	125.2, 125.4
P−N−C (in CH$_2$)[b]	116.1, 116.1	115.6, 115.6	116.3, 116.5	116.3, 115.9
N−C−C[b]	107.9, 107.7	108.9, 108.8	106.9, 106.5	107.3, 107.6

[a] The C atom is cis to the phosphenium ligand. [b] Parameters in the phosphenium ring.



(a) *facial* isomer (b) *meridoinal* isomer

Figure 1. Facial and meridional isomers of [(bpy)(CO)$_3$M{PNN}]$^+$ with C_s symmetry.

CH$_2$O}] (OSO$_2$CF$_3$)·CH$_2$Cl$_2$ (**2**).[6d] In both cases, the phosphenium ligand has a planar geometry. Complex **1** has Mo, P, and two N's in a plane. Similarly, complex **2** has Mo, P, N, and O in a plane. Therefore, we first postulate a planar phosphenium geometry for both facial and meridional isomers of [(bpy)(CO)$_3$Mo{PNN}]$^+$. Since the phosphenium plane may rotate around an M−P axis, many rotational isomers are conceivable. We started to carry out ab initio calculations on rotamers containing a high molecular symmetry. There are two possible rotamers with Cs symmetry for both facial and meridional isomers (see Figure 1). One has a phosphenium plane on a σ-plane (*fac*(0) and *mer*(0)) and the other has a phosphenium plane perpendicular to the σ-plane (*fac*(90) and *mer*(90)).

Preliminary single-point energy calculations on two facial isomers, *fac*(0) and *fac*(90), at the RHF/STO-3G level have been performed using experimental and/or assumed geometric parameters for the appropriate complexes such as **1**. It revealed that their total energies were comparable, and *fac*(0) was slightly, by 1 kcal/mol, more stable than *fac*(90). On the basis of this preliminary exploration, *fac*(0) was next subjected to full geometry optimizations at the RHF level of theory. To examine the basis set dependency on geometries and total energies, calculations were carried out with the following basis sets or ECPs: STO-3G, LANL2MB, and SKBJ(d). Table 1 lists the selected optimized geometric parameters for *fac*(0) together with the experimental parameters for **1**.[6d]

The agreement between the calculated and experimental structures is fairly good. The discrepancy between them for bond distances is less than 0.1 Å except for the several cases estimated using LANL2MB. STO-3G underestimated the bond distances, while LANL2MB and SKBJ(d) overestimated those parameters. The bond angles as well as the bond distances calculated by LANL2MB have the largest discrepancies among the three. One of the important aims of this study is to investigate the nature of an M−P(phosphenium) bond. Since the SKBJ(d) basis set results in better agreement between experimental and calculated Mo−P and P−N bond distances, the geometric parameters for the ligands were fixed to the optimized values with SKBJ(d) in the limited geometry optimization described in the following section.

Since *mer*(90) was estimated to be lower in energy by 18 kcal/mol than *mer*(0) in the preliminary single-point energy calculations at the RHF/STO-3G level, further full geometry optimization for *mer*(90) was performed with the same three basis sets as for *fac*(0). The *mer*(90) isomer was estimated to be more stable than the *fac*(0) isomer by 8.0, 9.9, and 6.4 kcal/mol in energy, as listed in Table 2, which is consistent with the experimental observation that the facial isomer spontaneously isomerizes to the meridional one. To consider electron correlation in this system, B3LYP/3-21G* energies were calculated at the RHF/SKBJ(d) geometry.[17] A relative energy of −6.3 kcal/mol for *mer*(90) versus f*ac*(0) by B3LYP/3-21G* is comparable to the calculated value, −6.4 kcal/mol, by RHF/SKBJ(d) calculations, as shown in Table 2. Computational values at the RHF level of theory are discussed in the rest of this paper.

The optimized structures of *fac*(0) and *mer*(90) with SKBJ(d) are drawn in Figures 2a and 2b, respectively. The X-ray-determined structure of **1** is shown in Figure 3 for comparison. Table 3 lists the detailed geometric parameters for *fac*(0) and *mer*(90).

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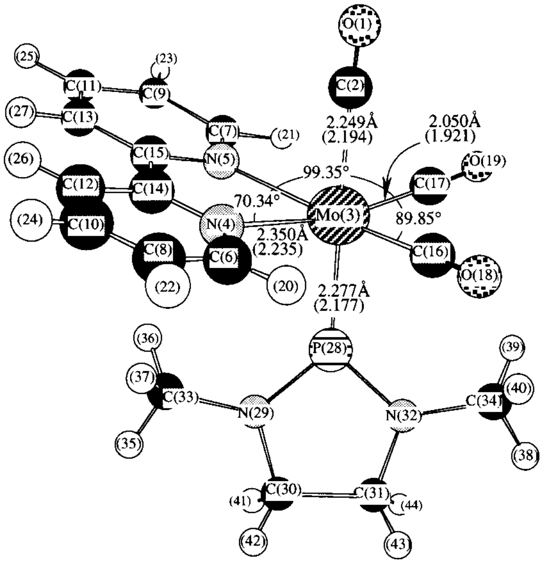
(17) For the importance of electron correlation in quantum chemical calculations of TM complexes, see the review: Frenking, G.; Antes, I.; Bohme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. *Rev. Comput. Chem.* **1996**, *8*, 63.

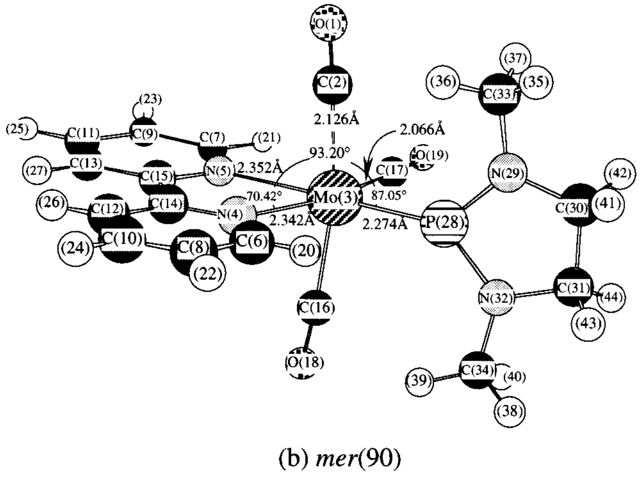
Table 2. Relative Energies (kcal/mol) among the Four Isomers with C_s Symmetry

method	central metal atom	*fac*(0)	*fac*(90)	*mer*(0)	*mer*(90)	Δ (*mer*(0)−*mer*(90))
Full Geometry Optimization						
RHF/STO-3G//RHF/STO-3G	Mo	0.0			−8.0	
RHF/LANL2MB//RHF/LANL2MB	Mo	0.0			−9.9	
RHF/SKBJ(d)//RHF/SKBJ(d)	Mo	0.0			−6.4	
Limited Geometry Optimization Concerning the Central Metal and Its Ligating Atoms[a]						
RHF/STO-3G	Mo	0.0	−2.2	16.2	−5.5	21.7
RHF/LANL2MB	Mo	0.0	−0.5	5.9	−9.3	15.2
	W	0.0	−1.1	6.6	−10.5	17.1
RHF/LANL2DZ	Mo	0.0	0.3		−3.8	
Single-Point Energy Calculations						
RHF/LANL2DZ//RHF/LANL2MB	Mo	0.0	1.1	8.6	−3.5	12.1
	W	0.0	0.2	9.5	−5.5	15.0
RHF/3-21G*//RHF/LANL2MB	Mo	0.0	0.9	9.5	−2.9	12.4
B3LYP/3-21G*//RHF/SKBJ(d)	Mo	0.0			−6.3	

[a] The geometric parameters for the ligands in facial and meridional forms were fixed to the optimized values of *fac*(0) and *mer*(90), respectively, at the RHF/SKBJ(d) level of theory.



(a) *fac*(0)



(b) *mer*(90)

Figure 2. Fully optimized structures of the *fac*(0)-Mo and *mer*(90)-Mo complexes at the RHF/SKBJ(d) level of theory. The values in parentheses in part a are optimized geometric parameters calculated at the RHF/STO-3G level.

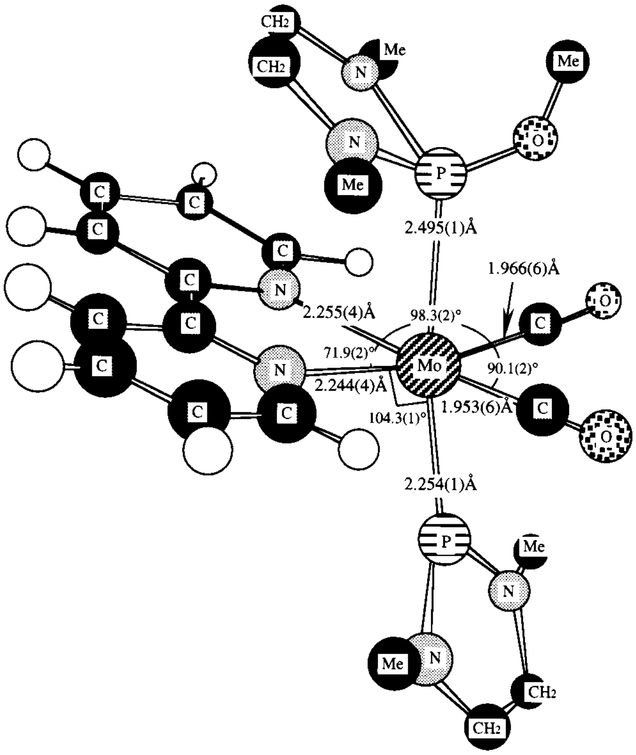


Figure 3. X-ray-determined structure of **1**.[6d]

Let us examine the structures obtained for *fac*(0) and *mer*(90) in detail. Both *fac*(0) and *mer*(90) have pseudo-octahedral geometries around Mo. The phosphenium phosphorus adopts a planar geometry for both *fac*(0) and *mer*(90), though the planarity in *fac*(0) is due to the symmetry. With *fac*(0), Mo, bpy, and two CO ligands trans to bpy are located in one plane, and P(28), Mo(3), and C(2) are arranged almost linearly (angle P(28)−Mo(3)−C(2) = 177.98°). The N(5)−Mo(3)−P(28) angle is slightly larger than 90° (98.08°) presumably due to the steric hindrance between bpy and the phosphenium ligand. With *mer*(90), Mo, bpy, C(17)O(19), and P(28) form a plane because of the symmetry adopted in this calculation. The two mutually trans CO ligands are slightly bent away from the phosphenium (angle C(2)−Mo(3)−C(16) = 170.21°) presumably due to steric repulsion.

fac(0) has two kinds of CO ligands: one is C(17)O(19), or equivalently C(16)O(18), trans to bpy, and the other is C(2)O(1) trans to the phosphenium. The Mo(3)−C(17) bond distance (2.050 Å) is shorter than the Mo(3)−C(2) bond distance (2.249 Å), while the C(17)−O(19) bond distance (1.139 Å) is longer than the C(2)−O(1) bond distance (1.123 Å). The results can be

Table 3. Fully Optimized Geometric Parameters of *fac*(0)- and *mer*(90)-[(bpy)(CO)$_3$Mo{PNN}]$^+$ at the RHF Level of Theory with the Basis SKBJ(d)

	fac(0)	*mer*(90)
Bond Distances between Metal and Ligands in Å		
Mo(3)−P(28)	2.277	2.274
Mo(3)−N (4)	2.350	2.342
Mo(3)−N (5)	2.350^a	2.352
Mo(3)−C (2)	2.249	2.126
Mo(3)−C(16)	2.050	2.126^a
Mo(3)−C(17)	2.050^a	2.066
Bond Distances in the Ligands in Å		
(phosphenium ligand)		
P(28)−N(29)	1.640	1.648
N(29)−C(30)	1.470	1.468
N(29)−C(33)	1.468	1.462
C(30)−C(31)	1.546	1.544
P(28)−N(32)	1.637	1.648^a
N(32)−C(31)	1.471	1.468^a
N(32)−C(34)	1.472	1.462^a
(bpy ligand)		
N(4)−C(6)	1.334	1.335
C(6)−C(8)	1.397	1.397
C(8)−C(10)	1.400	1.400
C(10)−C(12)	1.400	1.400
C(12)−C(14)	1.404	1.404
C(14)−N(4)	1.342	1.342
C(14)−C(15)	1.506	1.505
N(5)−C(7)	1.334^a	1.335
C(7)−C(9)	1.397^a	1.397
C (9)−C(11)	1.400^a	1.398
C(11)−C(13)	1.400^a	1.400
C(13)−C(15)	1.404^a	1.403
C(15)−N(5)	1.342^a	1.343
(CO ligands)		
C(2)−O(1)	1.123	1.130
C(17)−O(19)	1.139	1.137
Angles in deg		
C(2)−Mo(3)−P(28)	177.97	94.75
C(17)−Mo(3)−C(16)	89.85	91.43
C(2)−Mo(3)−C(16)	88.16	170.21
N(4)−Mo(3)−C(17)	167.41	163.62
N(4)−Mo(3)−C(2)	83.59	87.31
N(5)−Mo(3)−C(16)	167.41^a	85.25
N(5)−Mo(3)−P(28)	98.08	180.00
N(4)−Mo(3)−N(5)	70.34	70.42
N(5)−Mo(3)−C(17)	99.35	93.20
N(5)−Mo(3)−C(2)	83.59^a	85.25^a
C(2)−Mo(3)−C(17)	88.16^a	91.43^a
Dihedral Angles in deg		
C(7)−N(5)−Mo(3)−C(17)	7.84	0.00^b
C(7)−N(5)−Mo(3)−C(2)	94.91	−91.17
C(7)−N(5)−Mo(3)−P(28)	−83.90	0.00^b
C(6)−N(4)−Mo(3)−C(17)	−144.29	180.00^b
C(6)−N(4)−Mo(3)−C(2)	−94.91^a	−94.09

[a] Equivalent to another parameter due to the symmetry. [b] Fixed parameters because of the symmetry.

reasonably understood supposing that the phosphenium is a strong π-acceptor ligand. In *mer*(90), the bond distance of Mo(3)−C(2) is 2.126 Å, which is significantly shorter than that of Mo(3)−C(2) in *fac*(0) (2.249 Å). The former CO is trans to another CO ligand, and the latter is trans to the phosphenium ligand. Therefore, the calculated results are consistent with our understanding that the π-acceptability of the phosphenium ligand is stronger than that of a CO ligand. The bond distances between the Mo and a phosphenium phosphorus are almost the same for *fac*(0) and *mer*(90).

Relative Energies of Four Geometric Isomers of Mo and W Complexes. To estimate relative energies among *fac*(0), *fac*(90), *mer*(0), and *mer*(90) for Mo and W, geometry optimizations on them have to be performed. However, due to financial and time restriction for full geometry optimizations on our phosphenium complexes involving 26 atoms except hydrogens, the structures of the ligands, i.e., bpy, CO, and PNN in the facial and meridional isomers, were fixed to those obtained by RHF/SKBJ(d) full geometry optimizations for *fac*(0) or *mer*(90), respectively. The bond distances between the central transition metal and ligating atoms have been optimized using several computational methods. The relative energies thus obtained are listed in Table 2. The results of the full geometry optimization and those of single-point energy calculations are also listed.

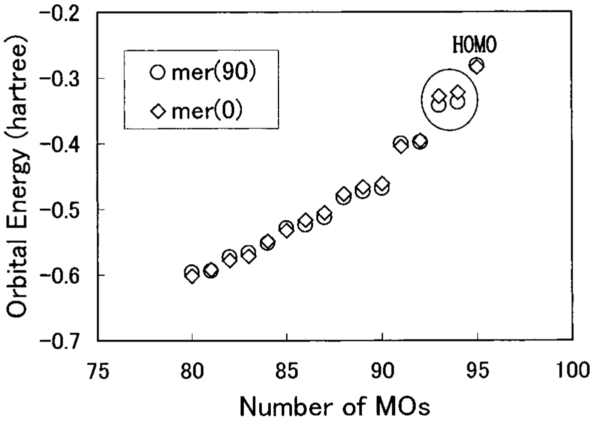


Figure 4. Energy level diagram for the occupied orbitals of the two meridional isomers, *mer*(90) and *mer*(0), of the Mo complex at the RHF/LANL2MB level. The data for the second and third HOMOs are marked with a large circle.

The relative energies obtained here depend to some extent on the computational scheme, the basis sets, and the ECPs used for optimization, but some tendencies can be extracted from Table 2. The energy difference between the two facial isomers, *fac*(0) and *fac*(90), is only 2 kcal/mol, regardless of the kind of central metal. This small energy difference agrees well with the experimental results from the X-ray diffraction method that complex **1** exhibits a geometric configuration close to *fac*(90), whereas complex **2** shows a geometric configuration similar to *fac*(0) in the solid state. In contrast, there is a substantial energy difference (12−22 kcal/mol) between *mer*(0) and *mer*(90), with *mer*(90) found to be more stable. The stability of the *mer*(90) form is consistent with the experimental observation that the two methyl carbons in the phosphenium ring are identical spectroscopically in meridional forms.[18] The reason for the large energy difference between *mer*(0) and *mer*(90) will be discussed in the next section.

Energy Levels and Shapes of Frontier Molecular Orbitals. In contrast with the small energy difference between *fac*(0) and *fac*(90), there is a significant energy difference between *mer*(0) and *mer*(90) for both the Mo and W complexes studied in this paper. The coplanarity of the phosphenium ring to bpy in the *mer*(0) form had seemed to be preferable because of π-conjugation between them. However, it was found that *mer*(90) is more stable than *mer*(0). To obtain a clue, the energy levels of the MOs of *mer*(0) and *mer*(90) were compared. The energy level diagram is shown in Figure 4 for the Mo complexes as an example. For occupied orbitals there

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[18] Yamaguchi Y. Ph.D. Dissertation; Hiroshima University, 1996.

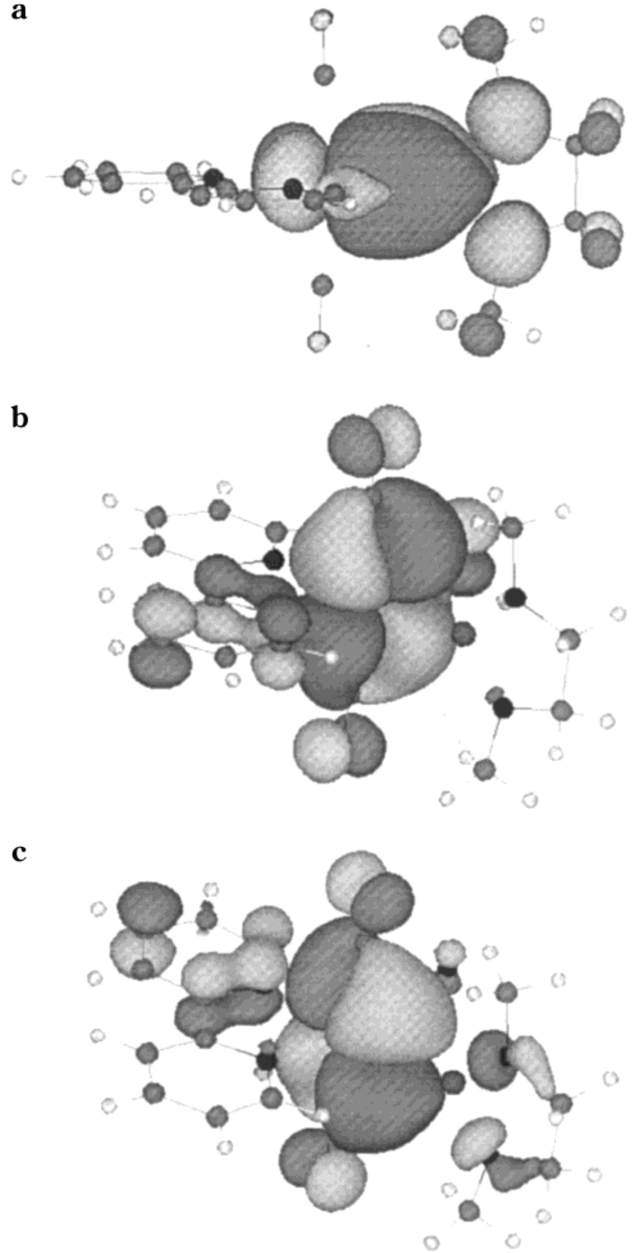

Figure 5. HOMO (a), second HOMO (b), and third HOMO (c) of the *mer*(90)-Mo complex at the RHF/LANL2MB level.

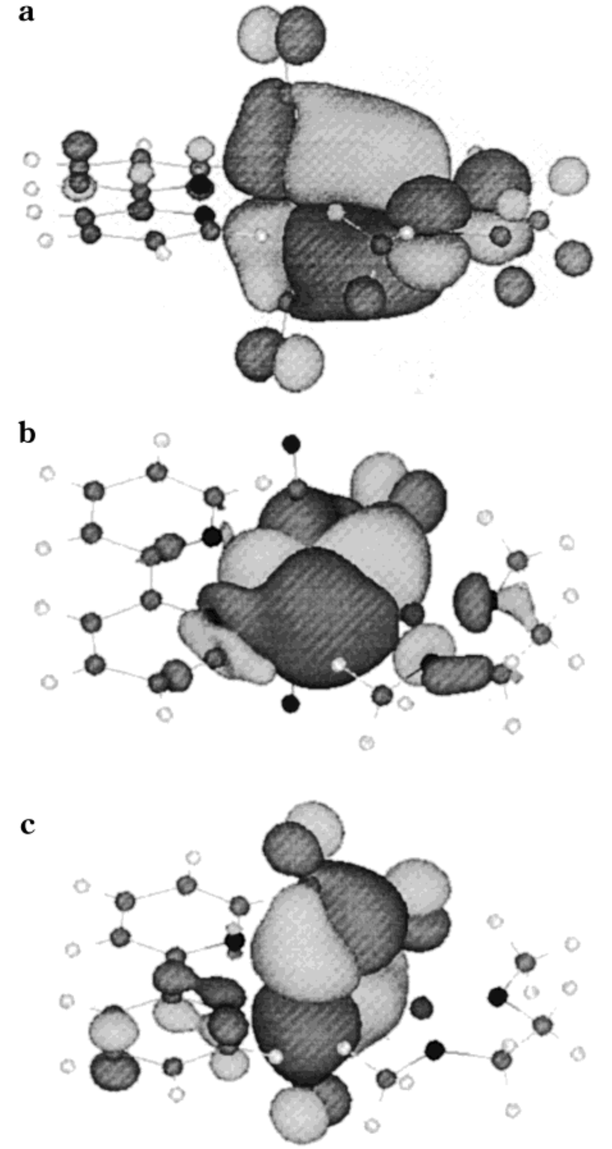

Figure 6. HOMO (a), second HOMO (b), and third HOMO (c) of *mer*(0)-Mo complex at the RHF/LANL2MB level.

is little difference between them except for the second and third HOMOs. The pictorial features of the HOMO and second and third HOMOs are shown in Figures 5 and 6. The HOMOs of *mer*(90) (Figure 5a) and *mer*(0) (Figure 6a) clearly depict the π-back-donation from a filled d orbital to an empty p orbital of the phosphenium phosphorus. The energy levels of the HOMOs are almost the same, as shown in Figure 4. The second HOMO of *mer*(90) (Figure 5b) is similar to the third HOMO of *mer*(0) (Figure 6c), and the third HOMO of *mer*(90) (Figure 5c) is similar to the second HOMO of *mer*(0) (Figure 6b). It is noteworthy that the third HOMO of *mer*(90) and the second HOMO of *mer*(0) correspond to π-back-donation from a filled d orbital of a transition metal to P−N σ antibonding (σ*) orbitals of the phosphenium ligand, and the third HOMO of *mer*(90) is more delocalized than the second HOMO of *mer*(0). Delocalization may be one of the means of stabilizing this molecular orbital. This third HOMO contributes to the stabilization of the *mer*(90) form, which may lead to the energy difference between mer(0) and mer(90).

M−P(phosphenium) Bond Character. To elucidate the characteristics of a phosphenium ligand on a transition metal, a comparison between the optimized geometry of a free phosphenium and that of a transition-metal-bound phosphenium might be beneficial. Thus, we have carried out geometry optimizations on $[\mathrm{PN(Me)\text{-}CH_2CH_2NMe}]^+$ at the same level of theory, RHF/SKBJ-(d), as employed for transition metal phosphenium complexes.

The metal-free phosphenium ring adopts an almost planar geometry with C_2 symmetry: The CH_2CH_2 moiety is slightly puckered with a dihedral angle of less than 5°. The sp^2 hybridization on the two N's indicates π-donation of the nitrogen lone pair to an empty p orbital of the phosphenium phosphorus.

A comparison of P−N bond distances is interesting. Those in *fac*(0) and *mer*(90) are almost the same (1.637−1.648 Å), but they are considerably longer than that for the metal-free phosphenium (1.604 Å). This can be

Table 4. Net Charges of Component Atoms in the Central Part of the Facial and Meridional Isomers at the RHF/LANL2MB Level

	Mo				W				free phosphenium[a]	
	fac(0)	*fac*(90)	*mer*(0)	*mer*(90)	*fac*(0)	*fac*(90)	*mer*(0)	*mer*(90)	*fac*	*mer*
metal	−0.113	−0.146	−0.180	−0.125	−0.250	−0.282	−0.323	−0.258		
C(2)	0.318	0.319	0.312	0.318	0.325	0.327	0.319	0.323		
N(4)	−0.242	−0.243	−0.236	−0.248	−0.235	−0.236	−0.228	−0.241		
N(5)	−0.242	−0.243	−0.251	−0.249	−0.235	−0.236	−0.242	−0.241		
C(16)	0.292	0.295	0.312	0.318	0.299	0.304	0.319	0.323		
C(17)	0.292	0.295	0.291	0.296	0.299	0.304	0.295	0.306		
P(28)	0.393	0.401	0.415	0.367	0.442	0.445	0.468	0.410	0.724	0.717
N(29)	−0.412	−0.409	−0.404	−0.408	−0.410	−0.407	−0.403	−0.408	−0.361	−0.354
N(32)	−0.410		−0.404		−0.406		−0.402		−0.361	

[a] Mulliken analysis was performed based on single-point energy calculations using optimized geometric parameters of the phosphenium moiety in *fac*(0) and *mer*(90) complexes.

reasonably explained if a phosphenium phosphorus coordinating to a transition metal would get π-donation predominantly from a transition metal and little from amino substituents.

Mulliken charge analysis is also helpful in interpreting the nature of the phosphenium ligand. The charges obtained by using the partial geometry optimization at RHF/LANL2MB are listed in Table 4. It is noteworthy that the Mulliken charges assigned to N in the phosphenium ligand (N(29) and N(32)) are almost the same (ca. −0.41) regardless of the geometric isomers (fac, mer), rotational isomers (0°, 90°), or the kind of transition metals (Mo, W) selected. This similarity and the fact that the value of −0.41 is more negative than the Mulliken charge of N in a free phosphenium (ca. −0.35) are consistent with the above postulation that the amino nitrogens donate little π electron density to the phosphenium phosphorus in a transition metal complex, but they do to some extent in a free phosphenium.

Next, let us compare the Mulliken charges on P. Those in transition metal complexes are always less positive than that of a free phosphenium, indicating considerable π-back-donation from a transition metal d orbital to an empty p orbital of a phosphenium phosphorus. There are some tendencies among the isomers. Irrespective of the kind of transition metals (Mo, W), *mer*(90) has a less positive value by ca. 0.05 than the corresponding *mer*(0), and *fac*(0) has a slightly less positive value than *fac*(90). The absolute values of the Mulliken charge on P are dependent on the kind of transition metals. It is larger in a W complex than in an Mo complex for every case, *fac*(0), *fac*(90), *mer*(0), and *mer*(90). This indicates that M to P π-back-donation in an Mo complex is more than in a W complex. This conclusion is further strengthened by a comparison of the Mulliken charges of the metals. The charges for Mo and W are negative, and that for W is more negative than that of Mo.

To elucidate the π-back-donation in phosphenium complexes in detail, populations of the formally empty p_π orbital of the phosphorus atom in the free ligand and in the complex were compared (see Table 5). Less population on the N atom in the free ligand than in the complex (*fac*(0) and *mer*(90)) means more electron transfer from N to P in the former than in the latter. More population on the P atom in the complex (*fac*(0) and *mer*(90)) corresponds to π-back-donation from the central metal.

Table 5. Populations (RHF/SKBJ(d)) in π Orbitals on the Phosphenium Ring in *fac*(0) and *mer*(90) Forms of the Mo Complex in Comparison with Those for a Free Phosphenium Ring

atom	*fac*(0)	*mer*(90)	free
P	0.712	0.728	0.542
N	1.782	1.787	1.685

Rotational Energy Barriers. We attempted to estimate the rotational energy barrier height of the phosphenium ligand. The phosphenium ligand was rotated along the M−P bond (M = Mo, W) from 0° to 90° at 15° intervals with maintaining its planarity, and the potential energy of each rotamer was estimated by single-point energy RHF/LANL2MB calculations where the fully optimized parameters obtained above for *fac*(0) and *mer*(90) were used except for the rotational angle around the M−P bond. Figures 7a and 7b show the potential energies of a facial isomer relative to *fac*(0) and those of a meridional isomer relative to *mer*(90), respectively. Energies obtained by more precise partial geometry optimization (see Table 2) are shown as the solid points at 90° in Figure 7a and at 0° in Figure 7b. These energies are lower than those obtained by single-point energy calculations, as expected. This means that other points in the figure would become lower in energy to some extent if partial or full geometry optimization is employed. However, the trend shown in Figure 7 may be reliable.

Figure 7a shows that a facial form has two local minima at 0° and 90° during the M−P rotation. The energy difference between them is 2 kcal/mol. This energy profile shows that the phosphenium ligand tends to have a staggered orientation, i.e., *fac*(0) or *fac*(90), rather than an eclipsed orientation, which corresponds to *fac*(45). This tendency has been demonstrated for transition metal complexes of carbene and its higher homologues, $(CO)_5Cr{=}EH_2$ (E = C, Si, Ge, Sn).[19] For *fac*-Mo and *fac*-W complexes, the rotational energy barrier height is, however, less than 2 kcal/mol, indicating that the phosphenium ligand rotates freely at thermal energies.

To examine whether steric effects of methyl groups connected to the N atoms in phosphenium ring affect the relative stability among facial and meridional isomers, the two methyl groups were replaced with two hydrogen atoms, and the rotational energies have been estimated for 45° and 60° rotamers. The results for facial forms of the Mo and W complexes are shown in Table 6 and illustrated as small solid marks in Figure

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[19] Jacobsen H.; Ziegler T. *Inorg. Chem.* **1996**, *35*, 775.

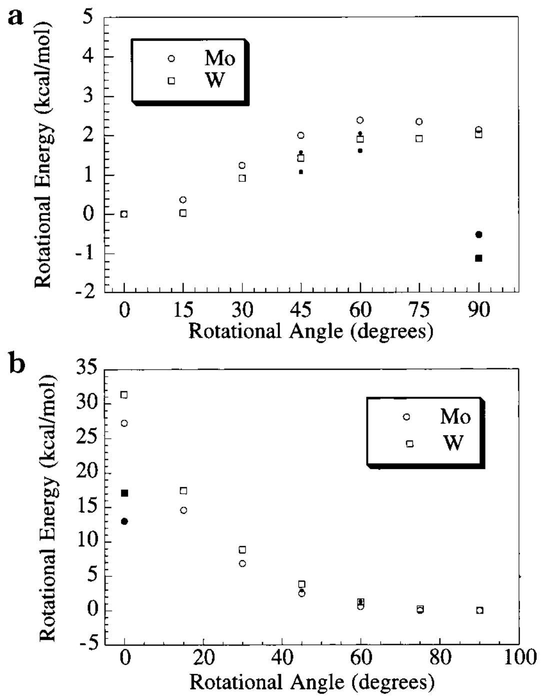

Figure 7. Potential energies of the Mo and W complexes for a facial isomer relative to *fac*(0) (a) and those for a meridional isomer relative to *mer*(90) (b) at the RHF/LANL2MB level: (i) the solid points at 90° (a) and at 0° (b) show the energies obtained by more precise partial geometry optimization (see Table 2), (ii) the small solid marks at 45° and 60° show the estimated values by considering the effect of a replacement of the methyl groups by H atoms.

Table 6. Effect of a Replacement of the Methyl Groups by H Atoms on the Potential Energies[a] (kcal/mol) of *fac*-$[(bpy)(CO)_3M\{\overline{PN(R)CH_2CH_2NR}\}]^+$ (R = Me, H; M = Mo, W)

M=	Mo		W	
R=	Me	H	Me	H
fac(0)	0.0	0.0	0.0	0.0
fac(45)	2.0	1.6	1.4	1.1
fac(60)	2.4	2.1	1.9	1.6

[a] Potential energy is relative to that of the corresponding *fac*(0).

Table 7. Effect of a Replacement of the Methyl Groups by H Atoms on the Potential Energies[a] (kcal/mol) of *mer*-$[(bpy)(CO)_3M\{\overline{PN(R)CH_2CH_2NR}\}]$ (R = Me, H; M = Mo, W)

M=	Mo		W	
R=	Me	H	Me	H
mer(0)	27.3	8.8	31.4	10.9
mer(45)	2.5	3.0	3.9	4.1
mer(60)	0.6	1.3	1.3	1.9
mer(90)	0.0	0.0	0.0	0.0

[a] Potential energy is relative to that of the corresponding *mer*(90).

7a. In all cases, the newly estimated values are lower than their counterparts, but the changes are very small (less than 1 kcal/mol). The following consideration is suggestive: A staggered orientation might be the best rotamer for a phosphenium to obtain π-back-donation from a transition metal to an empty p orbital of the phosphenium phosphorus, as is pointed out for carbene and its higher homologue.

Figure 7b shows the energy profile of phosphenium rotation for the meridional isomers. For Mo and W complexes, *mer*(90) is the minimum energy rotamer. This means that the meridional Mo and W complexes adopt an eclipsed orientation, which differs from the case of the corresponding facial isomer. The potential energy rises gradually on going from *mer*(90) to *mer*(45), and then it goes up rapidly to reach the maximum at 0°. The rotational barrier height is estimated to be 12−22 kcal/mol (see Table 2), indicating no free rotation of the phosphenium ligand at thermal energies. The computational results are consistent with the experimental findings that the two methyl and two methylene carbons in *mer*-[(bpy)(CO)$_3$M{PNN}]$^+$ have been observed to be equivalent in the ^{13}C NMR spectrum at room temperature,[18] although the possibility that the equivalence comes from phosphenium free rotation cannot be ruled out.

During the M−P rotation, steric hindrance between a methyl group in the phosphenium ligand and the bpy ligand is plausible. Thus, we have estimated the effect of a replacement of the methyl groups by H atoms on the potential energies for *mer*(0), *mer*(45), *mer*(60), and *mer*(90) of *mer*-[(bpy)(CO)$_3$M{PNN}]$^+$. The results are listed in Table 7 and illustrated as small solid marks in Figure 7b. With *mer*(0), substitution of Me with H causes ca. 20 kcal/mol lower relative energy to *mer*(90) irrespective of the transition metal, indicating that the high potential energy for *mer*(0) is due to steric hindrance between the bpy ligand and the Me groups in the phosphenium ligand. With *mer*(45) and *mer*(60), the relative potential energies to *mer*(90) of the H-substituted complexes are calculated to be slightly higher than those of the original complexes containing Me groups. This may be due to the application of single-point energy calculations. The potential energy of *mer*(90) is lower than that of *mer*(45) for both Me- and H-substituted complexes, although the difference is small.

In the case of the meridional isomer, the rotational energy is presumably on a critical balance between steric repulsion and π back-donation: *mer*(45) is the best orientation in terms of π-back-donation but has some steric repulsion between bpy and phosphenium; *mer*(90) is not the best orientation of π-back-donation but has the least steric repulsion. In fact, nuclear repulsion energies were estimated to be the smallest at the *mer*(90) form for the M−P rotation.

Concluding Remarks

Geometric features and energetics of facial and meridional isomers of cationinc phosphenium complexes of group 6 transition metals were interpreted based on ab initio MO calculations. The meridional isomer was estimated to be more stable in energy than the facial isomers, which agrees well with experimental behavior. Energy profiles in terms of phosphenium rotation along the M−P bond was also discussed. Those for the facial isomers revealed that *fac*(0) and *fac*(90) have similar thermodynamic stability and that the rotational energy barrier height was estimated to be less than 2 kcal/mol; thus the phoshenium ligand rotates freely at thermal energies. As for the meridional isomers, it was found that *mer*(90) was the minimum energy rotamer and that the meridional isomers seemed to have no free rotation of the phosphenium ligand at thermal energies due to the high rotational barrier height, which agrees well with the experimental findings.

Inspection of frontier molecular orbitals and Mulliken populations gave the clue to interpret the features of electronic structures and chemical bonding in the cationic phosphenium complexes of the group 6 transition metals.

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