by the lower symmetry $CrCl_3P_3$ environment.[17] The third spin-allowed d-d absorption band ν_3 ($^4A_{2g} \rightarrow {}^4T_{1g}$ (P)) is probably obscured by the intense chloride-to-metal charge-transfer transitions, which begin above 25 000 cm^{-1}.

An interesting question that arises is why the Cr(III) center forces the phosphine/chloride ligand set into a *mer* coordination geometry. The M-P bond distances in the related mononuclear complex *fac*-$Mo(CO)_3$(triphos) (triphos = $(Ph_2PCH_2CH_2)_2PPh$), for example, are at least as large as those seen for *mer*,*mer*-Cr_2Cl_6(eHTP), showing that a facial coordination geometry for **2** would be geometrically feasible.[18] According to Levason, a Cr(III) center has a relatively strong electronic preference for meridional coordination with halide and phosphine ligands.[6] Only when tripodal tris(phosphine) ligands were used (e.g., $MeC(CH_2CH_2PR_2)_3$), which are sterically forced to bind in a facial manner, were nonmeridional coordination geometries observed.[6,9] Suprisingly, Levason found that facial coordination was the preferred geometry for arsine ligands. The root cause of these electronic factors is not understood, and this represents a good case for molecular orbital calculations to shed further light on the matter.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8613089) and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Monsanto for a Young Faculty Research Support Grant.

Registry No. **2**, 110589-44-1.

Supplementary Material Available: Tables of hydrogen positional parameters, full bond distances and angles, and anisotropic thermal parameters and a figure of the IR spectrum for Cr_2Cl_6(eHTP) (8 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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[17] Other *mer*-MX_3L_3 complexes show substantial splittings in their d-d absorption bands in comparison to octahedral complexes. See, for example: Laier, T.; Schäffer, C. E.; Springborg, J. *Acta Chem. Scand., Ser. A* **1980**, *34A*, 343.

[18] Favas, M. C.; Kepert, D. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1980**, 447.

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CO_2 Rotational Isomerism in Bis(ethylene)(carbon dioxide)molybdenum Complexes: A Theoretical Study

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Received November 26, 1986

The organometallic chemistry of carbon dioxide has recently been the subject of numerous experimental studies, some emphasis being put on the synthesis of organic products of commercial interest.[1] In that respect the synthesis, by Carmona et al.,[2] of acrylic acid derivatives from the reaction of CO_2 with ethylene complexes of molybdenum and tungsten is especially attractive. The complex *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo, W) reacts with CO_2 to yield the dinuclear system $[M(H_2CCHCOOH)(C_2H_4)(PMe_3)_2]_2$, whose X-ray crystal structure indicates coupling of the ethylene and CO_2 ligands in the putative $M(C_2H_4)_2(CO_2)(PMe_3)_3$ intermediate. The knowledge of the structure of this intermediate is a prerequisite for understanding the coupling mechanism, which is presently unknown. From the X-ray crystal structures of the dinuclear product,[2] of the starting *trans*-$M(C_2H_4)_2(PMe_3)_4$ system,[3] and of the *trans*,*mer*-$Mo(C_2H_4)_2(CO)(PMe_3)_3$ complex,[3] one can reasonably infer that the phosphine ligands are in a meridional arrangement, leaving the two ethylene groups trans to each other (and staggered) and cis to the η^2-coordinated CO_2 ligand. It is more difficult, however, to assess the rotational isomerism around the M-CO_2 bond, which is also important for delineating the productive channels of the coupling reaction.

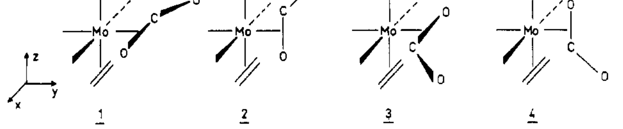
Table I. Relative Energies (kcal/mol) and Orbital Populations for Various Rotamers of the *trans*,*mer*-$Mo(C_2H_4)_2(CO_2)(PH_3)_3$ System

	1	**2**	**3**	**4**
rel energy	0	11.1	0	34.8
orbital pop.				
4s + $4d_\sigma$	1.38	1.29	1.38	1.25
$4d_{xy}$	1.02	1.86	1.02	1.86
$4d_{xz}$	1.51	1.50	1.51	1.45
$4d_{yz}$	1.56	0.84	1.56	1.04
net charge of Mo	+0.09	+0.10	+0.09	+0.13
net charge of CO_2	-0.51	-0.49	-0.51	-0.45

We therefore undertook a theoretical analysis of this problem, and we report here the results of LCAO-MO-SCF ab initio calculations[4] carried out on various conformers of the *trans*,*mer*-$Mo(C_2H_4)_2(CO_2)(PH_3)_3$ model system. The relative stabilities of the rotamers are then analyzed in terms of molecular orbital interactions.

Results and Discussion

For the *trans*,*mer*-$Mo(C_2H_4)_2(CO_2)(PH_3)_3$ system we consider four rotamers, which we denote **1-4** and which correspond to the rotation of CO_2 around the axis going through the metal and the coordinated C-O bond.[9] The corresponding relative energies of



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[1] For recent reviews, see for instance: (a) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651. (b) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

[2] Alvarez, R.; Carmona, E.; Cole-Hamilton, D. J.; Galindo, A.; Gutierrez-Puebla, E.; Monge, A.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1985**, *107*, 5529.

[3] Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014.

[4] The ab initio calculations were carried out with the Asterix system of programs[5] and the following Gaussian basis sets: (15,10,8) contracted to [6,4,4] for molybdenum,[6] (9,5) and (11,7) contracted to [3,2] and [4,3] for the first- and second-row atoms, respectively,[7] and (4) contracted to [2] for hydrogen.[8] The contracted basis set is minimal for the inner shells, double ζ for the valence shells, and triple ζ for the 4d of molybdenum.

[5] Bénard, M.; Daniel C.; Dedieu, A.; Demuynck, J.; Rohmer, M. M.; Strich, A.; Wiest, R.; Veillard, A. "Asterix", a system of programs, unpublished work. Bénard, M. *J. Chim. Phys.* **1976**, *73*, 413.

[6] Veillard, A.; Dedieu, A. *Theor. Chim. Acta* **1984**, *65*, 215.

[7] Huzinaga, S. "Approximate Atomic Functions"; Technical Report; University of Alberta: Edmonton, Alberta, Canada, 1971.

[8] Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

[9] The geometries were chosen as follows: A pseudooctahedral symmetry was assumed, and the Mo-P bond lengths were set to 2.50 Å.[3] The experimental geometry of PH_3[10] was retained. For the $Mo(C_2H_4)_2$ moiety, the Mo-C(ethylene) distances were set to 2.28 Å.[3] The C-C and C-H bond lengths were fixed at 1.40 and 1.10 Å, respectively, keeping a local pseudo-C_{3v} symmetry around the carbon atoms with the local C_3 axis making an angle of 80° with the C-C bond. The bond lengths of the Mo-CO_2 moiety were set according to the X-ray crystal structure of $Mo(CO_2)_2(PMe_3)_3(CN$-*i*-$Pr)$[11,12] (i.e., Mo-C = 2.105 Å, Mo-O = 2.147 Å, C-O = 1.258 and 1.22 Å for the coordinated and noncoordinated C-O bonds, respectively, and O-C-O = 133.5°) and kept fixed throughout the calculations. The orientation of CO_2 in its coordination plane was optimized however, by varying the angle made by the metal-carbon bond and the main axis going through the metal and the coordinated CO bond (the *y* axis), the optimized values being respectively 16.1, 13.2, and 19.6° for **1**, **2** and **4**. This procedure can be considered as being roughly equivalent to a simultaneous optimization of the kinking and of the slipping of CO_2. For a theoretical explanation of these deformations, we refer the reader to the work of Mealli et al.[13]

[10] Sirvetz, M. H.; Weston, R. E., Jr. *J. Chem. Phys.* **1953**, *21*, 898.

[11] Alvarez, R.; Carmona, E.; Gutierrez-Puebla, E.; Marin, J. M.; Monge, A.; Poveda, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 1326.

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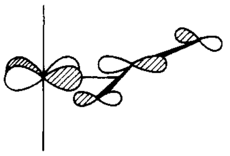
the isomers are given in Table I,[14] including data for **3** which is an enantiomer of **1**. Structure **1** appears to be the most stable. Also, whereas the interchange between **1** and **3** is rather easy through the rotation of CO_2,[15] further rotating of CO_2 back to **1** through **4** appears to be a difficult process.

The greatest stability of **1** is traced to an optimum set of interactions between the occupied d_π orbitals of molybdenum (d_{xy}, d_{xz}, d_{yz}) and the unoccupied π^* orbitals of the two ethylene groups and of the CO_2 ligand. In this case, and in this case only, each of the d_π orbitals interacts separately with the empty π^* ligand orbital of appropriate symmetry (see **5**–**7**). These interactions provide an important stabilization of the three d_π orbitals.



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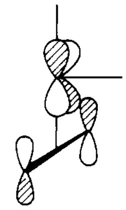

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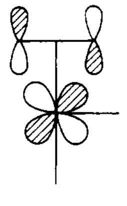

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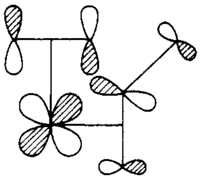
On the other hand, in **2**, the in-plane π^* orbital of CO_2 has to share the d_{yz} orbital of molybdenum with the π^* orbital of one of the ethylene ligands (see **8**). The additional stabilization of the d_{yz} orbital is not enough to compensate for the loss of stabilization of d_{xy}, which does not interact with any of the in-plane π^* orbitals of the C_2H_4 and CO_2 ligands. One may of course argue that d_{xy} receives some stabilization from the out-of-plane $\pi^*_{CO_2}$ orbital (see **9**), since the greater lobe on the carbon leads to some positive overlap. The overlap is much smaller however, leading to a much smaller stabilization. Moreover a similar interaction is also found in isomer **1** with d_{yz} (see **10**). Hence, the interaction with the out-of-plane $\pi^*_{CO_2}$ orbital does not differentiate, to an appreciable extent, isomers **1** and **2**.



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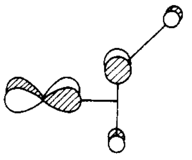

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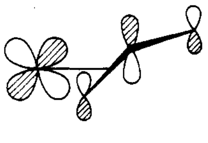

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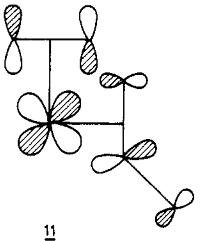
The populations of the d_π orbitals also reflect the above discussion (see Table I): from **1** to **2**, the loss of π back-donation that originates from $4d_{xy}$ (0.84) is not compensated by the gain in π back-donation arising from $4d_{yz}$ (0.72). As a result, the net charge on the CO_2 unit is decreased. The corresponding change is small however, due to a weaker σ donation of the ligands in **2** (this is best seen from the population of the Mo 4s and $4d_\sigma$, i.e. $4d_{z^2}$ and $4d_{x^2-y^2}$, orbitals, which decreases from **1** to **2**).

The rationalization of the greater stability of **1** as compared to that of **2** is therefore based on arguments that are now well-known[16] and that have been used in the study of bis(ethylene),[17] bis(carbene),[18] and carbene–ethylene[19] complexes. A salient feature of the rotational isomerism of these *mer*-$(C_2H_4)_2(CO_2)$ complexes, however, is the high destabilization of conformation **4** with respect to **1** and **2**. The rationale for this high destabilization does not lie only in the consideration of the through-bond stabilizing interactions: the through-bond stabilizing interactions **6** and **11** are rather similar to the ones found in conformation **2** (namely **6** and **8**). We note however that **11** is slightly less favorable than **8** because of a smaller overlap. [This is again reflected in the population of the d_{yz} orbital (see Table I), which is greater in **4** than in **2**, therefore indicative of a weaker π back-donation in **4** compared to that in **2**]. But the destabilization also arises, to a great extent, from a through-space interaction (see **12**) between the π orbital of the upper ethylene ligand and the $n\pi$ orbital of CO_2. Since these orbitals are both occupied, the interaction is a four-electron destabilizing one. It is peculiar to conformation **4** and cannot occur in **2** because of the absence of a lobe on the central carbon atom in the $n\pi$ orbital of CO_2.[20]



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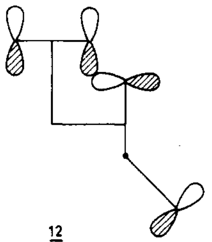

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(12) Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *106*, 2286.

(13) Mealli, C.; Hoffmann, R.; Stockis, A. *Inorg. Chem.* **1984**, *23*, 56.

(14) Total energies (in au): **1**, −5336.6915; **2**, −5336.6738; **3**, −5336.6915; **4**, −5336.6360.

(15) The conformation halfway between **1** and **2** (and between **2** and **3**) lies energetically between the two limit conformations, being destabilized by 0.9 kcal/mol only with respect to **1** (total energy of −5336.6900 au). As suggested by reviewer, this is probably indicative of a true energy minimum between **1** and the halfway structure. A parabolic fit indeed leads to a minimum for CO_2 being rotated by 18° from **1**. The energy gain is small however, 0.8 kcal/mol. Steric forces are probably at work here and might decrease when the $Mo(PH_3)_3(C_2H_4)_2$ framework is allowed to relax: we note that in the X-ray crystal structure of related systems[11,12] the metal–ligand bonds that are eclipsed with respect to the CO_2 ligand bend backward from CO_2. Yet the above results suggests that slight rotations of CO_2 from the equilibrium geometry are easy.

(16) (a) Rösch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656. (b) Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112.

(17) Bachmann, C.; Demuynck, J.; Veillard, A. *J. Am. Chem. Soc.* **1978**, *100*, 2366.

(18) Nakamura, S.; Dedieu, A. *Theor. Chim. Acta* **1984**, *64*, 461.

(19) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1986**, *108*, 2173.

(20) Steric arguments may be proposed to explain the destabilization of **4**. Yet **2** and **4** are rather similar in that respect. Furthermore, pilot SCF calculations were carried out for the model systems C_2H_4–CO_2 and C_2H_4–CN_2 for geometries corresponding to **2** and **4**, the geometry of the hypothetical CN_2 system being identical with that of CO_2. The only difference between the two systems is the absence of a doubly occupied $n\pi$ orbital in CN_2,[21] which prevents a four-electron destabilizing interaction with $\pi_{C_2H_4}$. It is therefore noteworthy that, for C_2H_4–CO_2, **4** is computed to be 10 kcal/mol less stable than **2**, whereas a reverse situation is found for C_2H_4–CN_2, **4** being more stable than **2** by 15 kcal/mol. This clearly illustrates the importance of the four-electron destabilizing interaction in the rotational isomerism of the η^2-CO_2 ligand.

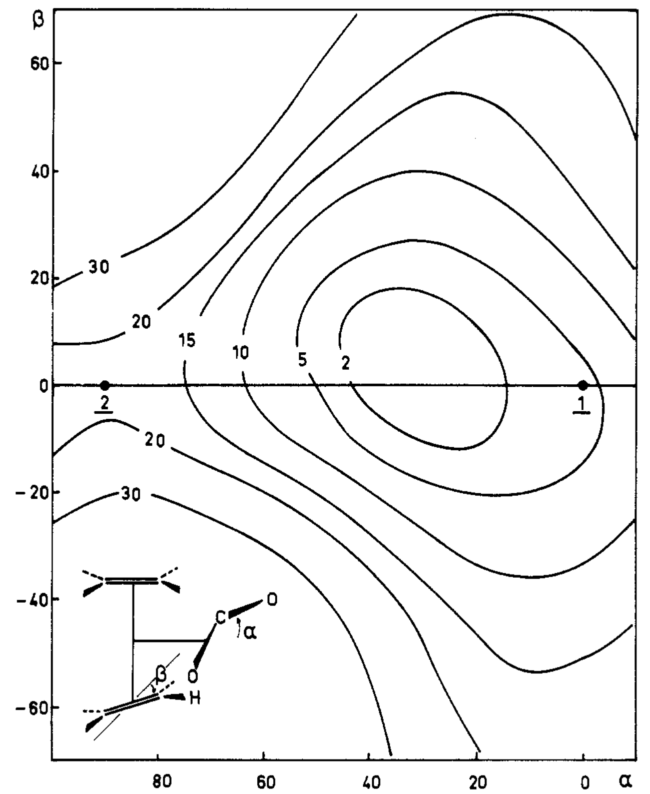

Figure 1. Potential energy surface obtained from extended Hückel calculations as a function of the CO_2 rotation angle α and the C_2H_4 rotation angle β (see the figure for the definition of α and β). $\alpha = 0°$ corresponds to isomer **1**, and $\alpha = 90°$, to isomer **2**. The contour values are in kcal/mol and refer to the energy minimum between **1** and **2** (i.e., $\alpha = 27°$ and $\beta = 0°$).

One finds here a distinctive feature of the rotational isomerism of η^2-coordinated CO_2 ligands, which should be operative in other cis olefin-η^2-CO_2 transition-metal complexes.

To what extent does the rotational isomerism described here influence the coupling of the C_2H_4 and CO_2 ligands? The determination of the corresponding reaction path lies beyond the scope of the present study. We note however that the structure of the acrylic acid derivative, which is the product of this coupling reaction, seems to originate from **1**, the C—O and $-CH{=}CH_2$ acrylic bonds being roughly parallel and the C—O bond being perpendicular to the $CH_2{=}CH_2$ double bond of the nonreacting coordinated ethylene (see the X-ray crystal structure in ref 2). Slight rotations of the CO_2 and/or of the C_2H_4 ligands, which require a few kcal-mol only,[15,22] bring a H atom close to the coordinated oxygen atom of the CO_2 ligand and may be involved at the beginning of the coupling. The corresponding potential energy surface, calculated at the EH level,[23] is repulsive however (see Figure 1). For a 60° rotation of CO_2 and a 40° rotation of C_2H_4 (this corresponds to an O–H distance of 1.92 Å, (i.e. still far from the equilibrium distance, which is close to 0.95 Å in acrylic acid), the destabilization with respect to the energy minimum amounts to 33 kcal/mol. This destabilization is the result of (i) the departure from the most stable arrangement of the two ethylene and the carbon dioxide ligands and (ii) four-electron repulsive interactions between the H s orbitals and both the out-of-plane $n\pi$ orbital of CO_2 and the σ framework orbitals of CO_2. The in-plane $\pi^*_{CO_2}$ orbital, which should accommodate the incoming hydrogen in this process, does not show any noticeable interaction with s_H. The O–H overlap population is negative (−0.02), hence underlying the nonbonding character of the interaction between the oxygen of CO_2 and the hydrogen of C_2H_4. We therefore do not favor a direct intramolecular hydrogen addition to the coordinated oxygen atom of the CO_2 ligand. Another alternative, which would account for the dinuclear nature of the product, is an intermolecular process: It involves the coupling of an ethylene bound to one molybdenum center with the CO_2 bound to a second molybdenum center and vice versa. In this case the attacked C–O bond is the noncoordinated one and the geometries of the two interacting molecules correspond to **1** and **3**. A final possibility[24] that would be more consistent with the hydrido acrylate formulation of the product (instead of the acrylic acid formulation[25]) might involve an intramolecular C–H oxidative addition followed by CO_2 insertion into the M–C bond of the resulting vinyl hydride intermediate. Clearly, the assessment of the coupling mechanism requires more work, which is now in progress.

Acknowledgment. Calculations were carried out on the IBM 3081 of the Centre de Calcul du CNRS in Strasbourg-Cronenbourg. V.B. is grateful to the CIRIT for financial support. We thank professor E. Carmona for his interest in this work.

Registry No. *trans,mer*-$Mo(C_2H_4)_2(CO_2)(PH_3)_3$, 110718-69-9.

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[21] The experimentally known cyanamide ion CN_2^{2-} is isostructural and isoelectronic with CO_2.

[22] Previous SCF calculations carried out on the $Mo(PH_3)_4(C_2H_4)_2$ system[17] have indicated that the barrier to overcome to go from the mutual staggered disposition of the two ethylene ligands to the mutual eclipsed disposition is of the order of 16 kcal/mol, the energy difference between the two limit conformations amounting to 13.9 kcal/mol. In the present case, extended Hückel calculations indicate a continuous increase in energy, up to 14 kcal/mol for the mutual eclipsed disposition of the two ethylene ligands.

[23] EH calculations were found to reproduce reasonably well the SCF calculations, the corresponding relative stabilities of **1**, **2**, and **4** being 0, 13.3, and 41.9 kcal/mol at the EH level. The most stable conformation at this level corresponds to CO_2 rotated by 27° from **1**, the corresponding stabilization amounting to 1.7 kcal/mol.

[24] This possibility was suggested to us by Prof. E. Carmona.

[25] See ref 10 of ref 2.

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Formation and Structure of the Bis(trimethylphosphine)nonahydrohexaboron(1+) Cation

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Received May 19, 1987

Earlier, we reported a series of polyboron complex cations with the formula $B_nH_{n+3}{\cdot}2P(CH_3)_3^+$, where n = 3, 4, and 5.[1-3] These cations are isostructural with their respective isoelectronic neutral and anionic species as illustrated in Figure 1. The next higher cation of series is $B_6H_9{\cdot}2P(CH_3)_3^+$, and its corresponding isoelectronic species are $B_6H_{10}{\cdot}P(CH_3)_3$ and $B_6H_{11}^-$, which are known to have the boron cluster geometry indicated in Figure 2a.[4,5] Abstraction of a hydride ion from $B_4H_8{\cdot}2P(CH_3)_3$ and $B_5H_9{\cdot}2P(CH_3)_3$ were the methods for preparing the above tetraboron and pentaboron complex cations, and the structures of these cations could readily be related with those of the parent bis(phosphine) adducts.[2,3]

The hexaboron cation would be obtainable likewise by abstracting a hydride ion from $B_6H_{10}{\cdot}2P(CH_3)_3$.

$$B_6H_{10}{\cdot}2P(CH_3)_3 + C(C_6H_5)_3^+ \rightarrow B_6H_9{\cdot}2P(CH_3)_3^+ + HC(C_6H_5)_3$$

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[1] Kameda, M.; Kodama, G. *J. Am. Chem. Soc.* **1980**, *102*, 3647.

[2] Kameda, M.; Kodama, G. *Inorg. Chem.* **1985**, *24*, 2712.

[3] Kameda, M.; Kodama, G. *Inorg. Chem.* **1987**, *26*, 2011.

[4] Kameda, M.; Kodama, G. *Inorg. Chem.* **1981**, *20*, 1072.

[5] Remmel, R. J.; Johnson, H. D., II; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.

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