*Tetrahedron* Vol. 42, No. 4, pp. 1109 to 1116, 1986
Printed in Great Britain.

0040-4020/86 \$3.00 + .00
Pergamon Press Ltd.

# Reactions of Organorhenium Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ with $Ph_3C^+\ PF_6^-$; Analysis of the Energetics of α-Hydride Abstraction

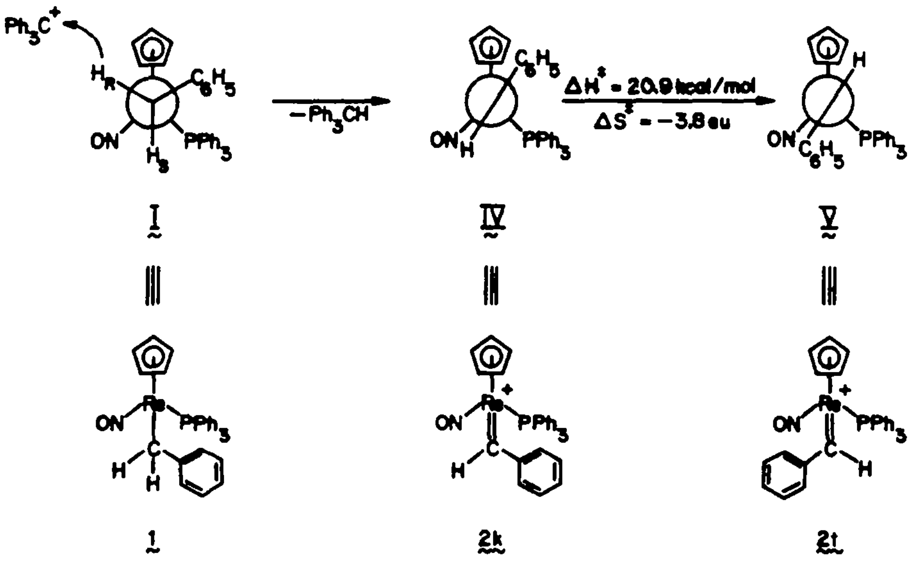
Savas Georgiou and J. A. Gladysz*
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

(*Received in USA* 3 *July* 1985)

**Abstract.** Reactions of $Ph_3C^+\ PF_6^-$ with rhenium alkyl complexes $(\eta^5\text{-}C_5H_5)$-$Re(NO)(PPh_3)(CH_2R)$ (R = phenyl, n-alkyl) give rhenium alkylidene complexes sc-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+\ PF_6^-$. Modifications in the energy-reaction-coordinate diagrams for these transformations are made on the basis of new data on the relative stabilities of the Re-$C_\alpha$ rotamers of the starting materials.

We have conducted a series of detailed studies of the reactions of rhenium alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2R)$ with the hydride abstraction agent $Ph_3C^+\ PF_6^-$.[1-5] When R = phenyl,[1] any n-alkyl,[2] or hydrogen,[3] α-hydride abstraction occurs to give an alkylidene complex sc-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+\ PF_6^-$ ("kinetic" or k isomer). Subsequently, Re=C bond

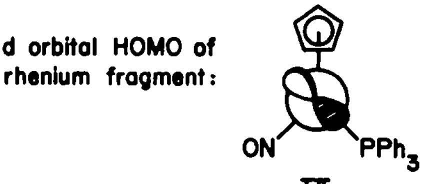
Scheme I. Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (1) with $Ph_3C^+\ PF_6^-$.



isomerization occurs (R $\neq$ H) to give a more stable geometric isomer, ac-[($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)(=CHR)]$^+$ $PF_6^-$ ("thermodynamic" or t isomer).

The stereochemistry of hydride abstraction from ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2C_6H_5$) (1) is illustrated in Scheme I. Studies with deuterium-labeled substrates (SS,RR)- and (SR,RS)-($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CHDC_6H_5$) have shown that $Ph_3C^+$ $PF_6^-$ abstracts essentially only the pro-R $\alpha$-hydride and that abstraction occurs from a direction anti to the $PPh_3$.[1] Similar experiments were conducted, and identical conclusions were reached, with n-alkyl complexes ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2R$).[2]

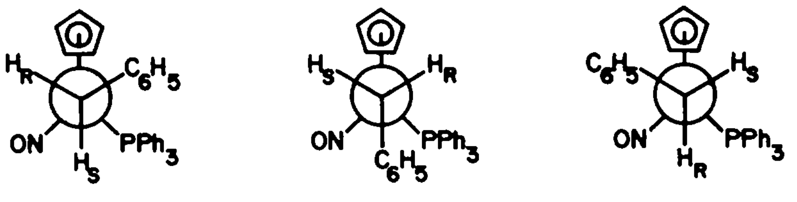
The HOMO of the ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)$^+$ fragment is the d orbital shown in VI.[1] Two lobes project out from the plane of the paper, and two lobes project behind. It is readily seen that in the preferred alkylidene ligand conformations (IV, V, Scheme I), overlap of this d orbital with the $C_\alpha$ p acceptor orbital is maximized. Hence, the HOMO should anchimerically assist the hydride abstraction process.



VI

At the time we reported the above data, one aspect of Scheme I surprised us. The reactive Re-$C_\alpha$ rotamer, I, had a $C_6H_5$ substituent situated between the two largest rhenium ligands, $PPh_3$ and $\eta^5$-$C_5H_5$. Hence, we considered it to be the least stable of the three possible Re-$C_\alpha$ rotamers (Scheme II). In the interim, Seeman and Davies published a new conformational analysis model for ($\eta^5$-$C_5H_5$)M(CO)($PPh_3$)($CH_2R$) and ($\eta^5$-$C_5H_5$)M(NO)($PPh_3$)($CH_2R$) complexes that is based upon structural and new theoretical data.[6,7] Baird has also studied the difference NOE spectra of these complexes.[8] Their results indicate that the least stable M-$C_\alpha$ rotamer is one in which the R group resides between the $PPh_3$ and NO or CO ligands, and that the most stable rotamer is one in which the R group resides between the $\eta^5$-$C_5H_5$ and NO or CO ligands (see II and III, Scheme II). We agree with these conclusions, and in this paper accordingly recast our analyses of the energetics of the preceding hydride abstraction reactions.

Scheme II. Re-$C_\alpha$ Rotamers of ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2C_6H_5$) (1).



I II III

## Results and Discussion

Scheme III shows a previously proposed[4] qualitative energy-reaction-coordinate diagram for the reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**1**) with $Ph_3C^+\ PF_6^-$ (Scheme I). Of particular note is the lack of reactivity of rotamer II. Abstraction of the hydride anti to the $PPh_3$ in II ($H_S$) would lead directly to the more stable Re=C product isomer, ac-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]^+\ PF_6^-$ (**2t**). To explain this result in the context of the Curtin-Hammett principle,[9] the hypothetical transition state connecting II and V was proposed to be of higher energy than the transition state connecting I and IV. Rotamer III is expected to be unreactive on stereoelectronic grounds: both $H_\alpha$ are nearly orthogonal to the rhenium d orbital HOMO (VI) used to form the Re=C π bond.

A revised energy-reaction-coordinate diagram is given in Scheme IV. Here, per the findings of Seeman, Davies, and Baird, the energies of rotamers I and II are inverted. The reactive rotamer is still I, as required by the labeling studies summarized above, and rotamer I still leads to the least stable of two possible products, IV. However, the greater reactivity of rotamer I is now easily rationalized (among several possibilities)[9] in the context of the Hammond postulate (reactant-like transition state) and from the fact that I will be present in greater concentration than II.

Scheme III. Previously Proposed Qualitative Energy-Reaction-Coordinate Diagram for the Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$ (**1**) with $Ph_3C^+\ PF_6^-$.

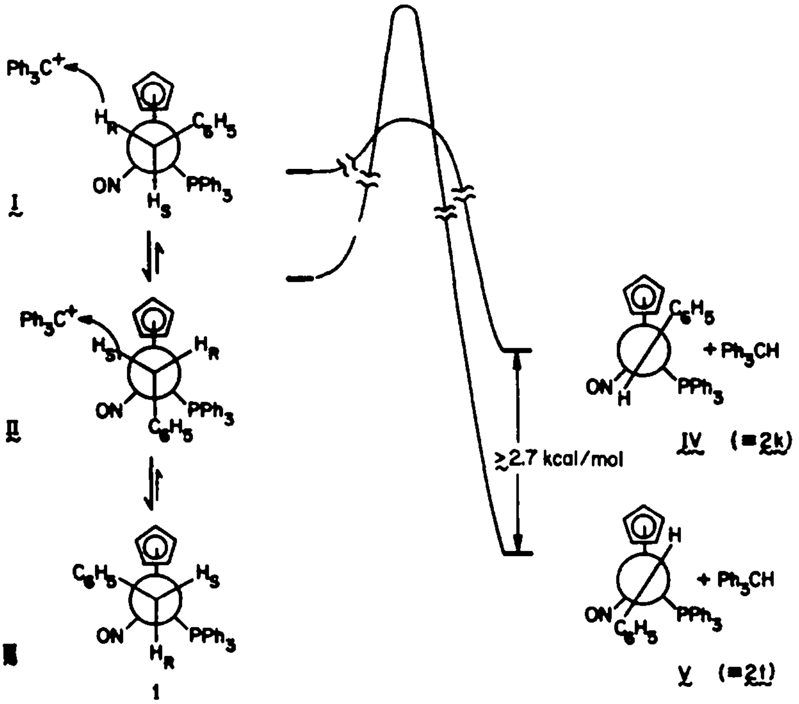


Figure 1. Variation in $E_{total}$ as the $CH_3$ ligand is rotated (A) in $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CH_3)$, and (B) in the corresponding radical cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CH_3)]^{+\bullet}$; calculated by the extended Hückel method ($\geq$1 data point/20°) with weighted $\underline{H}_{ij}$ formula. The calculated displacement of the two curves at $\theta = 40°$ is 11.87 eV.

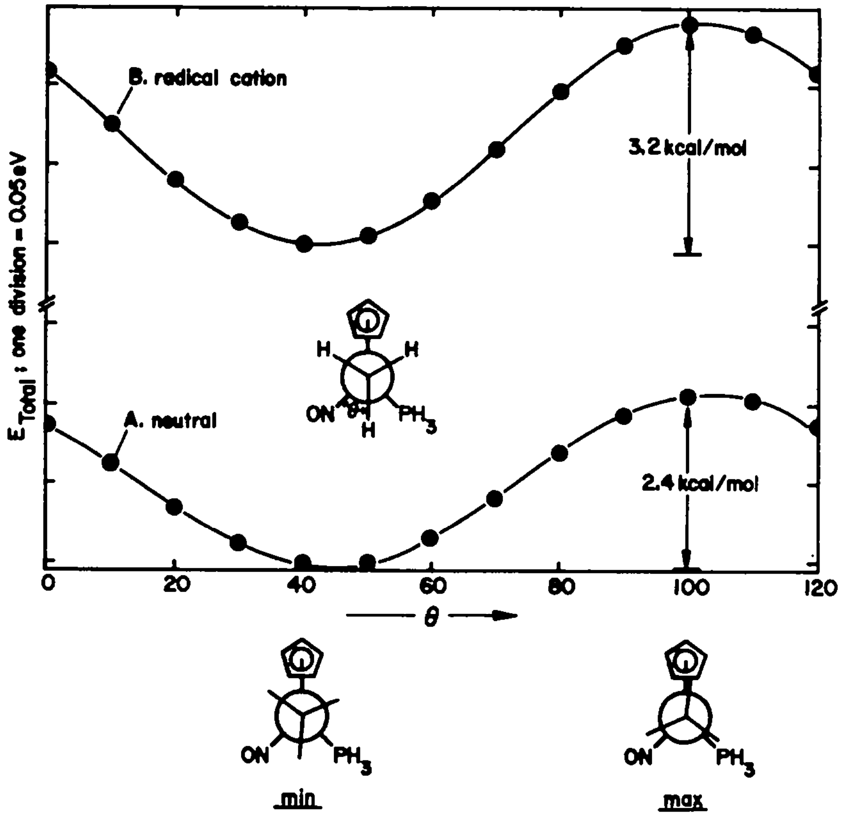
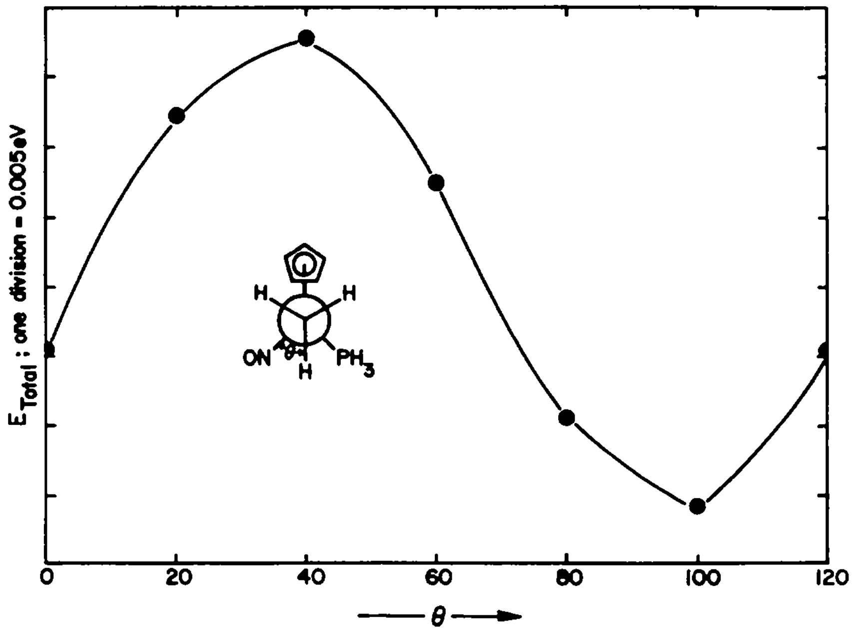


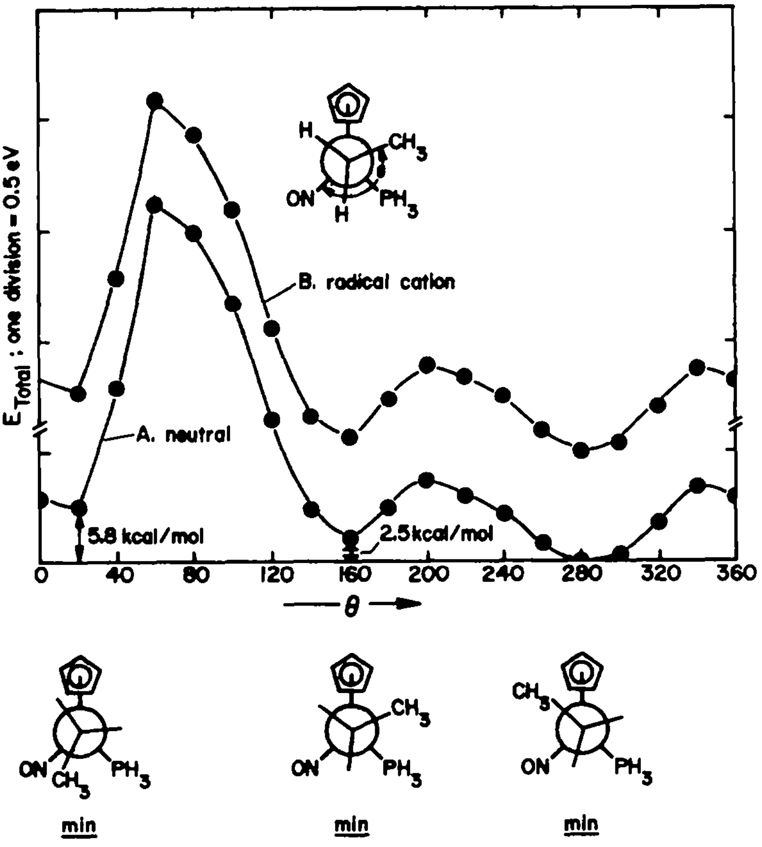
Figure 2. Variation in HOMO energy of $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CH_3)$ as the $CH_3$ ligand is rotated; calculated as in Figure 1.



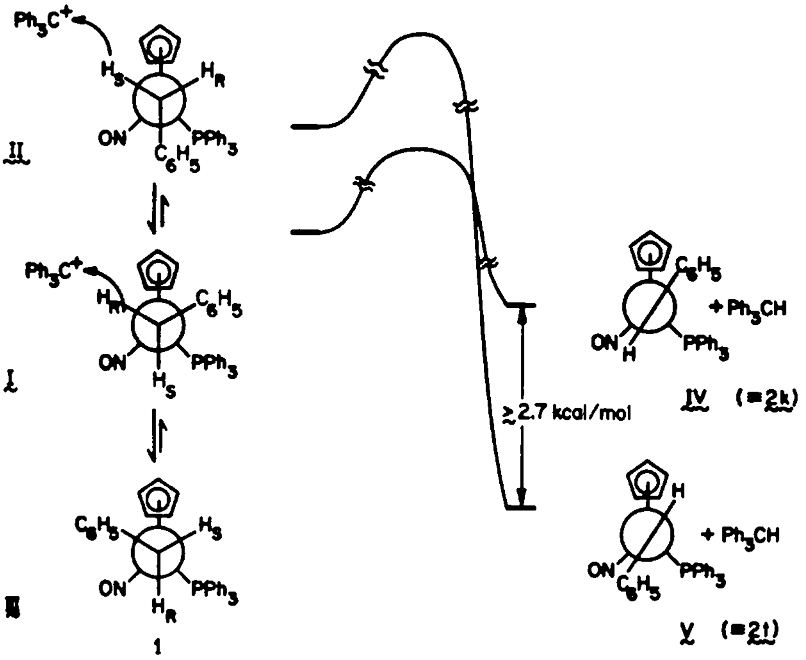
the HOMO (VI) -- i.e., the ionization potential. The energy of the HOMO of ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_3$) as a function of θ is given in Figure 2. In contrast to Figure 1, there is a maximum near θ = 40° and a minimum near θ = 100°. Thus, the slightly greater rotational barrier for the radical cation is due to the fact that the HOMO energy and $E_{total}$ of ($\eta^5$-$C_5H_5$)-Re(NO)($PH_3$)($CH_3$) run antiparallel to each other as a function of θ.

Figure 3 shows the variation in $E_{total}$ for the model ethyl complex ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)-($CH_2CH_3$), and the corresponding radical cation, as the Re-$C_\alpha$ bond is rotated. Extensive energy minimization was done for the former complex, and an identical geometry was assumed for the latter. Again, both energy-reaction-coordinate diagrams are very similar. The three Re-$C_\alpha$ rotamers of ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_2CH_3$) found as minima are shown at the bottom of Figure 3. Although we hesitate to interpret the small differences in calculated energy between these minima, we do compute a stability order corresponding (for benzyl complex 1) to III > I > II. Seeman and Davies have found that the calculated energy differences between these rotamers (and the energy barriers which connect them) are greatly enhanced when P($C_6H_5$)$H_2$ is substituted for $PH_3$.[6b]

Figure 3. Variation in $E_{total}$ as the $CH_2CH_3$ ligand is rotated about Re-$C_\alpha$ (A) in ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_2CH_3$), and (B) in the corresponding radical cation [($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_2CH_3$)]$^{+\cdot}$; calculated as in Figure 1.



Scheme IV. Revised Qualitative Energy-Reaction-Coordinate Diagram for the Reaction of ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2C_6H_5$) (1) with $Ph_3C^+$ $PF_6^-$.



We have also been actively concerned that hydride abstractions from alkyl complexes ($\eta^5$-$C_5H_5$)Re(NO)($PPh_3$)($CH_2R$) may occur via initial electron transfer.[5] Towards this end, it is important to question whether the relative energies of rotamers I-III, and their ease of interconversion, will be affected by oxidation to the corresponding radical cation. We have probed this question via extended Hückel MO calculations,[10,11] as outlined in the Experimental Section.

Figure 1 depicts the variation in $E_{total}$ for the model compound ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_3$) as the Re-$C_\alpha$ bond is rotated ($\theta$). An energy barrier of 2.4 kcal/mol (0.106 eV) is calculated. The corresponding graph for the radical cation $[(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CH_3)]^{+\cdot}$ (of identical geometry) is also shown. An energy barrier of 3.2 kcal/mol (0.139 eV) is calculated. For both curves, the maximum occurs near $\theta = 100°$ and the minimum at $\theta = 40°$-$45°$. Clearly, insofar as the extended Hückel method can detect, there is only a small change in the energy-reaction-coordinate diagram for Re-$C_\alpha$ bond rotation in ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_3$) upon oxidation, provided that the geometry of the resulting radical cation is as assumed.

The slight difference between the two curves in Figure 1 can be analyzed. In simple extended Hückel theory, the difference between $E_{total}$ for ($\eta^5$-$C_5H_5$)Re(NO)($PH_3$)($CH_3$) and the corresponding radical cation is equivalent (for any given $\theta$) to the negative of the energy of

In conclusion, our results are fully consistent with the recent data of Seeman, Davies, and Baird concerning relative M-$C_\alpha$ rotamer stabilities of $(\eta^5\text{-}C_5H_5)M(CO)(PPh_3)(CH_2R)$ and $(\eta^5\text{-}C_5H_5)M(NO)(PPh_3)(CH_2R)$ compounds. Some of the important aspects of estimating rotamer stabilities are, from our standpoint, as follows.

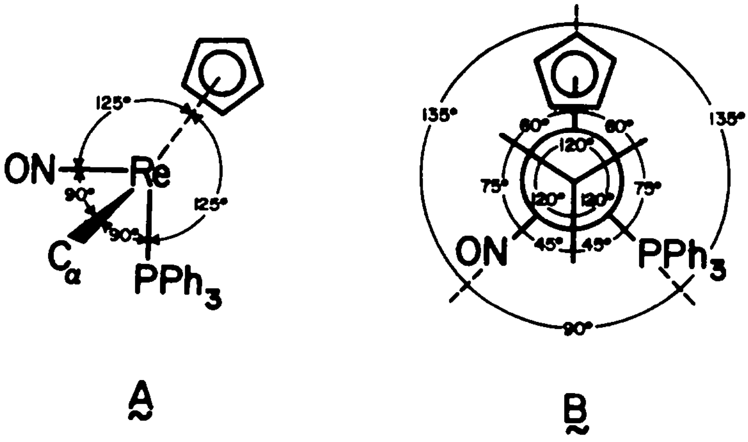
First, it is not sufficient to consider only ligand size when estimating the stabilities of M-$C_\alpha$ rotamers in LL'L"M-$CH_2R$ complexes. In rhenium complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$, the $PPh_3$ ligand is certainly the largest, the NO ligand is certainly the smallest, and the $\eta^5\text{-}C_5H_5$ ligand is therefore "medium". On this basis, rotamer II in Scheme II would (erroneously) appear to be more stable than I.

Second, the idealized angles defined by the ligands on the metal must be considered. In Figure 4, we give two views of the ligand geometries about rhenium in $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$-(CHRR') complexes. These perspectives are based upon the results of numerous X-ray crystal structures,[1,3,11,12] and have been rigorously adhered to in our previous full papers. View A shows the complex in three dimensions. View B is a Newman projection down the $C_\alpha$-Re bond for one staggered conformation. Note that in both perspectives, the angle or "bite" defined by ON-Re-$PPh_3$ (90°) is smaller than that defined by ON-Re-$(\eta^5\text{-}C_5H_5)$centroid and $(\eta^5\text{-}C_5H_5)$centroid-Re-$PPh_3$. This, we believe, is the critical factor in rationalizing the stability order I > II.

Finally, it is instructive to contrast view B with a Newman projection down the carbon-carbon bond of ethane. Unlike the latter, B can never be perfectly staggered or eclipsed. In addition, the hydrogens on the rear carbon of ethane extend further behind the plane of the rear carbon. In B, only the $\eta^5\text{-}C_5H_5$ centroid extends further behind the plane of the rhenium; the nitrogen and phosphorus are in the plane of the rhenium. Furthermore, X-ray data indicate that some $\eta^5\text{-}C_5H_5$ carbons extend to the plane of the rhenium ($\angle\, C_\alpha\text{-Re-}C_{Cp} \leq 90°$).

Hence, ordering the stabilities of M-$C_\alpha$ rotamers of LL'L"M-$CH_2R$ complexes is considerably more complex than ordering the stabilities of analogous $sp^3$-carbon-$sp^3$-carbon rotamers. Furthermore, the metal-carbon and other metal-ligand bond lengths involved vary widely. Thus,

Figure 4. Two views of the ligand geometries in $(\eta^5\text{-}C_5H_5)Re(NO)(PH_3)(CHRR')$ complexes.



the interplay of numerous factors must be considered, and it can be anticipated that this will develop into a particularly rich sub-field of conformational analysis.

## Experimental

Extended Hückel calculations were conducted with weighted $H_{ij}$ formula. The rhenium, phosphorus, and $sp^3$ carbon atoms were assigned idealized octahedral, tetrahedral and tetrahedral geometries, respectively. Bond lengths used were as follows (Å): Re-C, 2.10; Re-N, 1.78; N-O, 1.19; Re-P, 2.36; Re-$C_5H_5$, 2.33 (distance to carbon); C-C of $C_5H_5$, 1.40; C-C of $CH_2CH_3$, 1.54; C-H, 1.09; P-H, 1.44. For carbon, nitrogen, oxygen and hydrogen, the $H_{ii}$ and $\zeta$ previously reported by Hoffmann[10] were employed. The parameters utilized for rhenium and phosphorus were as follows: Re 6s, $H_{ii}$ = -9.36 eV, $\zeta$ = 2.398; Re 6p, $H_{ii}$ = -5.96 eV, $\zeta$ = 2.372; Re 5d, $H_{ii}$ = -12.66 eV, $\zeta$ = 5.343 (coefficient = 0.6359) and 2.277 (coefficient = 0.5677); P 3s, $H_{ii}$ = -18.6 eV, $\zeta$ = 1.6; P 3p, $H_{ii}$ = -14.0 eV, $\zeta$ = 1.6.

The same parameters were used for the calculations on radical cations. The energy of the ethyl complex was optimized by first varying the rotational structure of the $PH_3$ ligand and then the $C_\alpha$-$C_\beta$ rotational structure of the ethyl ligand. Only the conformations with $\theta$ = 40-100° (Figure 3) proved sensitive to the optimization procedure.

**Acknowledgement.** We thank the Department of Energy for support of this research, and Dr. J. I. Seeman and Professor S. G. Davies for a preprint of reference 6b.

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