

suggested by the prominence of *cis* products in eq 1. If the one-electron model is an accurate representation of the relative energies of the excited-state fragments, the results in eq 1 can still be explained by the stereochemical rearrangement model. If we arbitrarily set the rate constants pertaining to rearrangement as  $k_{ba} = 8k_{ab}$ , then the relative rate constants  $k_{ab} = 3.5k_{na}$ ,  $k_{ba} = 28k_{na}$ , and  $k_{nb} = 34k_{na}$  mimic the experimental values in eq 1. However, these results require that deactivation of  $SP_{\text{basal}}^*$  be much more rapid than deactivation of  $SP_{\text{axial}}^*$ .

The fact that the series of M(III) systems  $d^5$  Ru(III),<sup>9</sup>  $d^6$  Rh(III),<sup>3-7</sup> and  $d^6$  Ir(III)<sup>10</sup> show varying degrees of excited-state rearrangement when the  $[M(\text{en})_2\text{Cl}^{2+}]^*$  fragment is formed is not surprising. The ability to traverse the barrier in both directions ( $SP_{\text{apical}}^* \leftrightarrow SP_{\text{basal}}^*$ ) for Ru(III), in only one direction for Rh(III) ( $SP_{\text{basal}}^* \rightarrow SP_{\text{apical}}^*$ ), and only a small amount in one direction ( $SP_{\text{basal}}^* \rightarrow \text{some } SP_{\text{apical}}^*$ ) for Ir(III) can be linked to both the absolute magnitude of  $e_{\sigma}^i$  values ( $\text{Ir(III)} > \text{Rh(III)} > \text{Ru(III)}$ ) and the spin-orbit coupling constant ( $\text{Ir(III)} > \text{Rh(III)} \approx \text{Ru(III)}$ ) which should make  $k_{na}$  and  $k_{nb}$  larger for the third-row Ir(III).

The current experimental data on  $d^6$  system<sup>12</sup> of Rh(III)<sup>3-7</sup> and Ir(III)<sup>10</sup> are consistent with the stereochemical rear-

rangement model<sup>1,2</sup> and demonstrate the fine balance between the dynamic processes leading to rearrangement and deactivation. Of greater importance is the observation that differing *cis/trans* product ratios from photodissociation of Y from *cis*- and *trans*- $[MA_4XY]$  does not preclude the presence of a common set of five-coordinate intermediates. Lastly, initial data on the  $d^5$  Ru(III) systems<sup>9</sup> is compatible with the stereochemical model, although much more experimental work is needed to reinforce this point. However, the fact that the Vanquickenborne/Ceulemans model<sup>1</sup> may be applicable to  $d^5$  systems as well as  $d^3$  and  $d^6$  systems suggests that a unifying concept relating ligand field photosubstitution processes of  $d^n$  systems may be emerging.

Kinetic modeling of experimental data utilized a fourth-order Runge-Kutta integration of the rate equations on the Clemson University IBM 370/3033 computer. Initially, either  $SP_{\text{apical}}^*$  or  $SP_{\text{basal}}^*$  was given a unit concentration (all other concentrations were set at zero), and rate constants and reaction times were varied until at least 99% of the initial concentration appeared as ground-state  $SP_{\text{apical}}$  and  $SP_{\text{basal}}$ .

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(12) The kinetic treatment applied here can be used to analyze the photochemical reactions of the Co(III) analogues *cis*- $\text{Co}(\text{en})_2\text{Cl}_2^+$  (Sheridan, P. S.; Adamson, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 3032) and *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$  (Pribush, R. A.; Poon, C. K.; Bruce, C. M.; Adamson, A. W. *Ibid.* **1974**, *96*, 3027).

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## Additions and Corrections

1981, Volume 20

M. S. Delaney, C. B. Knobler, and M. F. Hawthorne\*: A Designed Metallocarborane Catalyst. Synthesis, Structure, and Reactions of [*closo*-1,3- $[\mu-(\eta^2-3\text{-CH}_2=\text{CHCH}_2\text{CH}_2)]-3\text{-H-3-PPPh}_3-3,1,2\text{-RhC}_2\text{B}_9\text{H}_{10}$ ].

Page 1347. In Table VI, under substrate, the second to last entry reads *3,3-dimethylbut-1-ene*. The correct entry should read *3,3-dimethylbut-1-yne*.—M. F. Hawthorne

1981, Volume 20

Edward H. Wong\* and Fontaine C. Bradley: Hydrolysis of Chlorodiphenylphosphine Complexes of Molybdenum and Palladium.

Page 2333. In Table I, the <sup>31</sup>P NMR chemical shift for *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_2\text{Cl})_2$  should be 126.4 ppm and that for *trans*- $(\text{CO})_4\text{Mo}(\text{PPh}_2\text{Cl})_2$  should be 137.4 ppm.—Edward H. Wong