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 $k_{\mathrm{ba}} = 8k_{\mathrm{ab}}$, then the relative rate constants $k_{\mathrm{ab}} = 3.5k_{\mathrm{na}}$, $k_{\mathrm{ba}} = 28k_{\mathrm{na}}$, and $k_{\mathrm{nb}} = 34k_{\mathrm{na}}$ mimic the experimental values in eq 1. However, these results require that deactivation of $\mathrm{SP}_{\mathrm{basal}}$* be much more rapid than deactivation of $\mathrm{SP}_{\mathrm{axial}}$*.

The fact that the series of M(III) systems $d^5$ Ru(III),[9] $d^6$ Rh(III),[3-7] and $d^6$ Ir(III)[10] show varying degrees of excited-state rearrangement when the $[\mathrm{M(en)_2Cl^{2+}}]^*$ fragment is formed is not surprising. The ability to traverse the barrier in both directions ($\mathrm{SP}_{\mathrm{apical}}^* \leftrightarrow \mathrm{SP}_{\mathrm{basal}}^*$) for Ru(III), in only one direction for Rh(III) ($\mathrm{SP}_{\mathrm{basal}}^* \rightarrow \mathrm{SP}_{\mathrm{apical}}^*$), and only a small amount in one direction ($\mathrm{SP}_{\mathrm{basal}}^* \rightarrow$ some $\mathrm{SP}_{\mathrm{apical}}^*$) for Ir(III) can be linked to both the absolute magnitude of $e_\sigma^{\,i}$ values (Ir(III) > Rh(III) > Ru(III)) and the spin–orbit coupling constant (Ir(III) > Rh(III) $\simeq$ Ru(II)) which should make $k_{\mathrm{na}}$ and $k_{\mathrm{nb}}$ larger for the third-row Ir(III).

The current experimental data on $d^6$ system[12] of Rh(III)[3-7] and Ir(III)[10] are consistent with the stereochemical rearrangement model[1,2] 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*-$[\mathrm{MA_4XY}]$ *does not* preclude the presence of a common set of five-coordinate intermediates. Lastly, initial data on the $d^5$ Ru(III) systems[9] 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[1] 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 fouth-order Runge–Kutta integration of the rate equations on the Clemson University IBM 370/3033 computer. Initially, either $\mathrm{SP}_{\mathrm{apical}}$* or $\mathrm{SP}_{\mathrm{basal}}$* 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 $\mathrm{SP}_{\mathrm{apical}}$ and $\mathrm{SP}_{\mathrm{basal}}$.

Department of Chemistry
Clemson University
Clemson, South Carolina 29631

**John D. Petersen**

*Received November 24, 1980*

---

(12) The kinetic treatment applied here can be used to analyze the photochemical reactions of the Co(III) analogues *cis*-$\mathrm{Co(en)_2Cl_2^+}$ (Sheridan, P. S.; Adamson, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 3032) and *trans*-$\mathrm{Co(en)_2Cl_2^+}$ (Pribush, R. A.; Poon, C. K.; Bruce, C. M.; Adamson, A. W. *Ibid.* **1974**, *96*, 3027).

---

# Additions and Corrections

1981, Volume 20

**M. S. Delaney, C. B. Knobler, and M. F. Hawthorne***: A Designed Metallacarborane Catalyst. Synthesis, Structure, and Reactions of $[closo\text{-}1,3\text{-}[\mu\text{-}(\eta^2\text{-}3\text{-}\mathrm{CH_2{=}CHCH_2CH_2})]\text{-}3\text{-}\mathrm{H}\text{-}3\text{-}\mathrm{PPh_3}\text{-}3,1,2\text{-}\mathrm{RhC_2B_9H_{10}}]$.

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 $^{31}$P NMR chemical shift for *cis*-$\mathrm{Mo(CO)_4(PPh_2Cl)_2}$ should be 126.4 ppm and that for *trans*-$\mathrm{(CO)_4Mo(PPh_2Cl)_2}$ should be 137.4 ppm.—Edward H. Wong