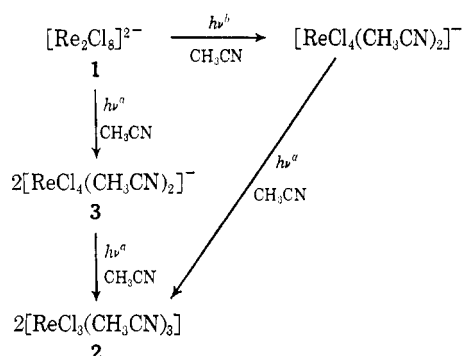


Table I. Infrared and Electronic Spectral Data for Compounds 1–3

Compound	$\nu_{\text{Re-Cl}}$, cm^{-1}	Electronic absorption maxima, ^a nm
$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ (1)	333 ^b	680, 370, 353, 309, 252
$[\text{ReCl}_3(\text{CH}_3\text{CN})_3]$ (2)	^c	310 sh, 275, 245, 230
	315 ^d	
	293 ^d	
$[(\text{CH}_3)_3\text{NH}][\text{ReCl}_4(\text{CH}_3\text{CN})_2]$ (3)	^c	315 sh, 271, 255, 232
	301 ^d	

^a In CH_3CN solution. ^b Nujol mull. ^c Bands at 2970, 2911, 1405, 1355, 1015, 939, and 720 cm^{-1} are attributable to coordinated CH_3CN . ^d KBr disks.

Scheme I

^a $366\text{ nm} \geq \lambda > 300\text{ nm}$. ^b $\lambda 254\text{ nm}$.

filtered excitation is 3, but 3 is then further photolyzed to 2. $[\text{ReCl}_3(\text{CH}_3\text{CN})_3]$ is isolated in higher yield because of the much greater quantum yield of the second photolysis compared to the first. $[\text{ReCl}_4(\text{CH}_3\text{CN})_2]^-$ is also the primary photoproduct under higher energy (254 nm) excitation, although in this case the spectral changes are very complex, indicating secondary and tertiary photoreactions. A chromatographic separation of a partially 254-nm photolyzed solution on silica gel produces a small amount of a tan compound whose uv-visible and ir spectra are identical with those of 3 and that when photolyzed with Pyrex-filtered light produces 2.

$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ does not react with CH_3CN when stored in the dark or when kept under reflux for 12 hr, indicating that Re_2 cleavage occurs in an electronic excited state. The quantum yield of disappearance of $[\text{Re}_2\text{Cl}_8]^{2-}$ was found to be independent of the intensity of the exciting light,¹⁶ suggesting that a one-photon process is responsible. Surprisingly, irradiation of 1 in CH_3CN with a He-Ne laser (632.8 nm) does not lead to reaction, which means that bond cleavage occurs from one of the excited states higher than that derived from the $\delta \rightarrow \delta^*$ transition. Cleavage is observed when solutions are irradiated at 366 nm, which is in the region of $\sigma \rightarrow \delta^*$ absorption.

Although we cannot present a detailed mechanism for the excited-state cleavage of Re_2 , the fact that the reaction occurs at all has important implications concerning the characteristics of the quadruple bond. Previous bond-energy estimates in the range 300–400 kcal/mol^{5,17} seem unreasonably high. If the mechanism involved simple dissociation to ReCl_4^- , photolysis at 366 nm would place an upper limit of 78 kcal/mol on the bond

dissociation energy. However, the solvent undoubtedly plays an important role in the reaction and may lower the effective dissociation energy below that of the free ion. Such lowering could not be attributed to classical ionic solvation energy, as dissociation converts a doubly charged anion to two singly charged species. However, the monomeric ion is probably bound much more strongly than the dimer to acetonitrile molecules. If $[\text{Re}_2\text{Cl}_8]^{2-}$ is weakly bound to two acetonitrile molecules oriented along the Re-Re axis in the ground state, these molecules may become tightly bound and aid dissociation of the excited state. We do not believe that more complex reorganization of the system can be involved since the reaction must occur during the very short lifetime of an upper excited state. It would be extraordinarily difficult to imagine interactions of this kind with the solvent which would lower the dissociation energy by more than 50 kcal/mol. Consequently, we doubt that the Re_2 bond energy in the dimer can exceed 130 kcal/mol.

Acknowledgments. We thank the Army Research Office (Durham) for support of this research. Certain items of equipment were obtained through a grant from the National Science Foundation.

Gregory L. Geoffroy, Harry B. Gray*

Contribution No. 4838

Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology, Pasadena, California 91109

George S. Hammond

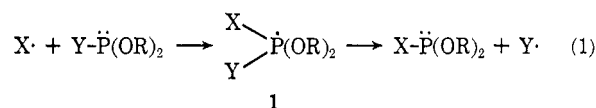
Division of Natural Sciences, University of California
Santa Cruz, California 95060

Received February 19, 1974

Stereochemistry of Free-Radical Displacements at Trivalent Phosphorus

Sir:

We wish to report the first study of the stereochemistry of a free-radical displacement at trivalent phosphorus (reaction 1). Although such displacements



do occur at various heteroatoms in organometallic and organometalloid systems, their stereochemistries are rarely determined.¹ Furthermore, displacements at trivalent phosphorus are of special interest because of the considerable *a priori* possibility that they may proceed with retention of configuration. Extensive amounts of chemical² and esr evidence³ suggest that

(1) K. U. Ingold and B. P. Roberts, "Free-Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971. To our knowledge the only examples of truly free radical displacements whose stereochemistries are known are those on carbon in strained systems. For a recent example see J. H. Incremona and C. J. Upton, *J. Amer. Chem. Soc.*, **94**, 301 (1972).

(2) W. G. Bentrude and T. B. Min, *J. Amer. Chem. Soc.*, **94**, 1025 (1972); W. G. Bentrude and R. A. Wielesek, *ibid.*, **91**, 2406 (1969).

(3) See, e.g., P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6033 (1972); G. B. Watts, D. Griller, and K. U. Ingold, *ibid.*, **94**, 8784 (1972); A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, *J. Organometal. Chem.*, **40**, C33 (1972); W. Nelson, G. Jackel, and W. Gordy, *J. Chem. Phys.*, **52**, 4572 (1970); R. W. Fessenden and R. H. Schuler, *ibid.*, **45**, 1845 (1966); G. F. Kokoska and F. E. Brinckman, *J. Amer. Chem. Soc.*, **92**, 1199 (1970).

(16) The intensity experiment was conducted using the 1000-W Hg-Xe lamp equipped with neutral density filters having an absorbance of 0.3, 0.6, and 1.2.

(17) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 924 (1967).

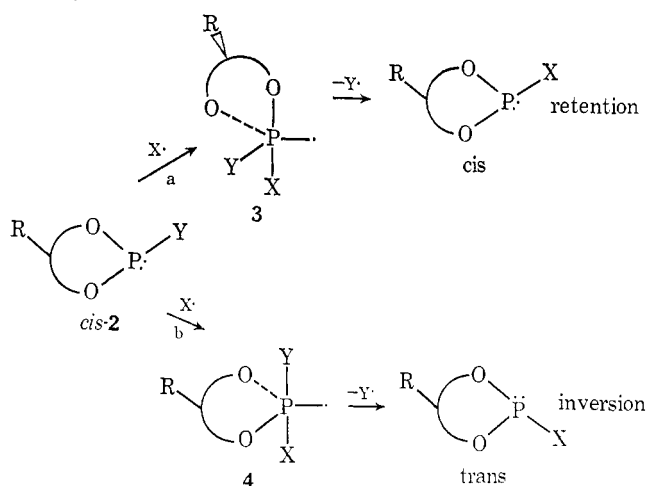
Table I. Reactions of Dimethylamino Radicals with **5a** and **5b**^a

Reactant	Cis/trans initial	Cis/trans consumed	Trans/cis- 5c formed	% cis- 5a or 5b consumed	% trans- 5c formed	% trans- 5a or - 5b consumed	% cis- 5c formed	% yield total 5c
5a	65/35	78/22	77/23	35	38	21	21	99
	48/52	73/27	72/28	44	39	15	14	92
	36/64	59/41	60/40	50	47	20	18	92
	6/94	10/90	43/57	50	400	30	15	75
5b	87/13	79/21	80/20	27	26	50	44	94
	62/38	46/54	48/52	25	25	47	43	95
5c ^b	46/54		71/29 ^c					84

^a Solutions were 0.5 ml in volume, 0.2–0.4 M in **5a** and **5b** in benzene. Ratio of tetrazene/**5a** or **5b** = 1.2–1.8. Reactants **5a** and **5b** was 30% consumed. ^b Ratio of **5c**/tetrazene was 1.0. ^c Tetrazene was <40% consumed.

free-radical reactions with trivalent phosphorus often proceed *via* an intermediate phosphoranyl radical, **1**, an expanded valence shell species of trigonal bipyramidal geometry with the odd electron equatorial. Thus in reaction (Scheme I) of a cyclic species such as *cis*-2

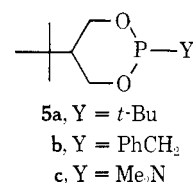
Scheme I



with $\text{X}\cdot$, if one assumes an axial introduction of $\text{X}\cdot$ into the initial phosphoranyl radical,⁴ two initial structures, **3** or **4**, could result. As is clearly shown in Scheme I, the two routes lead to *opposite* overall displacement stereochemistries. Most notably, pathway **a** results in retention.⁵ To the extent that intermediates like **3** and **4** resemble truly pentacoordinate species, one would expect that the comparative ease of formation of **3** or **4** and hence the stereochemistry of a displacement process like eq 1 would depend on the electronegativity and $p\pi$ - $d\pi$ bonding abilities of the substituents X and Y ⁶ and also be influenced by the steric requirements⁴ of ring systems attached to phosphorus.

The specific systems we have studied involve the displacement of an alkyl substituent (Y) on phosphorus by a dimethylamino radical ($\text{X}\cdot$). In particular we have found that dimethylamino radicals, generated at 15° in degassed benzene on photolysis of the tetrazene

$\text{Me}_2\text{NN}=\text{NNMe}_2$ ⁷ (medium-pressure Hg lamp, Pyrex reaction tubes), react with *cis*/*trans* isomeric mixtures of the 2-*tert*-butyl- and 2-benzyl-5-*tert*-butyl-1,3,2-dioxaphosphorinanes, **5a** and **5b**, respectively, to yield the corresponding isomeric *cis* and *trans* phosphoramidites **5c** (2-dimethylamino-5-*tert*-butyl-1,3,2-dioxaphosphorinanes).



phosphorinanes).⁸ Both reactions proceed in >90% yields with high stereoselectivity and *predominant configurational inversion at the phosphorus site*.

Table I records results at 30% conversions for reactions of **5a** and **5b** for more than one initial *cis*/*trans* starting ratio of isomers. Data were taken from plots covering 70–80% reaction utilizing the *tert*-butyl pmr resonances of **5a** at δ 0.79 (*cis* isomer) and 0.60 (*trans* isomer) and of **5b** at δ 0.61 (*cis* isomer) and 0.72 (*trans* isomer) along with the *tert*-butyl peaks for product **5c** at δ 0.69 (*cis* isomer) and 0.64 (*trans* isomer). A known amount of anisole was added as internal standard. Results determined in this way were checked by a glc method in which **5a**, **5b**, and **5c** were first converted to the corresponding sulfides.⁹ Agreement between the two methods was excellent.

It is seen from Table I that for 65/35, 48/52, and 36/64 *cis*/*trans* ratios of **5a**, the ratio *cis*/*trans* of consumed **5a** is close to the inverse ratio, *i.e.*, *trans*/*cis*, for product **5c**. Also shown is the close correspondence between the per cent of total *cis*-**5a** which has undergone reaction and the per cent *trans*-**5c** formed. The latter figure is based upon total per cent *cis*-**5a** available for reaction (*i.e.*, (mmol *trans*-**5c** formed)/(mmol initial *cis*-**5a**) \times 100). Thus, *cis*-**5a** yields largely *trans*-**5c** while *trans*-**5a** gives predominately *cis*-**5c**.

Nonequilibrium¹⁰ *cis*/*trans* mixtures of **5c** are equili-

(7) W. C. Danen and T. T. Kensler, *J. Amer. Chem. Soc.*, **92**, 5235 (1970).

(8) The conformations and *cis* and *trans* geometries of the isomers of **5c** are well known. W. G. Bentrude and H.-W. Tan, *J. Amer. Chem. Soc.*, **95**, 4666 (1973). Those for **5a** and **5b** were determined by previously established methods (see above reference and W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *ibid.*, **93**, 797 (1971)). The *cis* and *trans* geometries of the **5a** isomers have been established unequivocally with the aid of X-ray crystallographic work on the corresponding sulfides by C. N. Caughlan and coworkers, Montana State University.

(9) Such oxidations are of known retentive stereochemistry in such systems and are often used to determine isomeric ratios of trivalent compounds. See, *e.g.*, ref 8.

(10) The equilibrium *cis*/*trans* ratio for **5c** in benzene at 25° is 17:83.

(4) Such an assumption is based on analogy to what is usually assumed in the formation of truly pentacoordinate systems. K. Mislow, *Accounts Chem. Res.*, **3**, 321 (1970); F. H. Westheimer, *ibid.*, **1**, 70 (1968); P. Gillespie, F. Ramirez, I. Ugi, and D. Marquarding, *Angew. Chem., Int. Ed. Engl.*, **12**, 91 (1973). For a review of phosphoranyl radical systems, see W. G. Bentrude in "Free Radicals," Vol. 2, J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, pp 595–663.

(5) If X and Y are similar enough to require (microscopic reversibility) that *both* enter and leave axially, then a simple pseudorotation (or its permutational equivalent) of **3** would put Y in the axial position.

(6) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970); R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **94**, 3047 (1972).

brated under the reaction conditions with partial consumption of **5c** (see last line of Table I). This is the likely reason that reaction of $\text{Me}_2\text{N}\cdot$ with 6/94 (thermodynamically equilibrated) *cis/trans* **5a** gives a poor correspondence between isomeric ratios of reacted **5a** and product **5c** as well as a poor yield of **5c**. The dominant *trans*-**5a** is less reactive than is *cis*-**5a**, hence dimethylamino radicals react rapidly with *cis*-**5c** leading finally to its equilibration with *trans*-**5c**. Note, however, that the *trans/cis* ratio for product **5c** from reaction of 6/94 **5a** is reduced as expected for an inversion pathway.

When **5b** is the reactant, the minor *trans*-isomer is the thermodynamically less stable form⁸ and the more reactive isomer toward $\text{Me}_2\text{N}\cdot$. The data again argue for *inversion about phosphorus as the predominant pathway*. Yields of $\text{PhCH}_2\text{CH}_2\text{Ph}$ as high as 80% attest to the free-radical nature of the displacement on **5b**.

We interpret these results (inversion) to mean that if a phosphoranyl radical is involved in these processes, its geometry must be such that X and Y are either coaxial or coequatorial. The attacking radical $\text{Me}_2\text{N}\cdot$ clearly is not introduced into the phosphoranyl intermediate in a configurationally random manner, a result consistent with earlier conclusions drawn from investigations of reactions of alkoxy radicals with trialkyl phosphites.² If as assumed above, $\text{X}\cdot$ enters the intermediate axially, and the odd electron is *equatorial*, then structure **4** will give the observed stereochemistry.

Since the alkyl substituents on phosphorus are relatively electropositive and according to esr results³ appear to exhibit an equatorial preference in the most thermodynamically stable form of intermediates such as $\text{Me}_3\text{PO}\cdot t\text{-Bu}$ and $\text{Me}_2\text{P}(\text{OR})_2$, kinetic factors may favor formation of **4**. Alternatively, the stereochemistry of these systems may be controlled by the presence of the six-membered ring which in pentacovalent systems has been suggested¹¹ to have a thermodynamic preference for diequatorial attachment to phosphorus. Finally, the particular systems investigated may react *via* a concerted (synchronous SH_2) mechanism. These possibilities are being investigated.

Acknowledgment. This research was generously supported by grants from the National Cancer Institute of Public Health Service (CA-11045) and by the National Science Foundation (GP-36637X1).

(11) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsois, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).

Wesley G. Bentrude,* Wajid A. Khan
Masashi Murakami, Han-Wan Tan

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

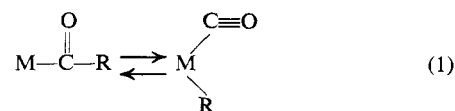
Received April 20, 1974

Direct Determination of the Enthalpy Change for the Migration of Para-Substituted Benzyl and Trifluoromethyl Groups in Coordinatively Unsaturated Iridium(III) Acyl Complexes

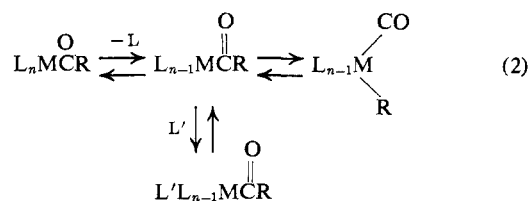
Sir:

The insertion of carbon monoxide into a metal-carbon bond or its reverse, the migration of an alkyl or aryl group from an acyl carbon to a metal site in an acyl complex, are of widespread occurrence in organo-

metallic syntheses and homogeneous catalytic processes.¹ A reaction sequence which accounts for what is known of the mechanism for these transformations is shown in



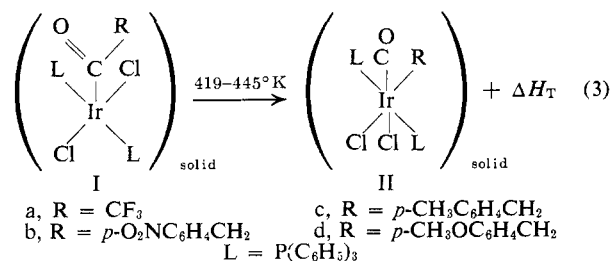
eq 2.¹ In general the intermediate of reduced coordi-



nation number, $\text{L}_{n-1}\text{MC}(\text{O})\text{R}$, is not detected and the actual migration (or insertion) step is not observed independent of the loss (or addition) of a ligand from the metal coordination sphere. It is not surprising, then, that no thermochemical data have yet been reported for the reaction step in which the alkyl or aryl group migrates to or from the coordinated CO group.

In 1971 Kubota, Blake, and Smith reported the synthesis of a series of five-coordinated phenylacetyl complexes of iridium(III).^{2a} These compounds were used as models for the coordinatively unsaturated intermediate in eq 2, and the rate of the migration step was studied.² We now wish to report that these five-coordinated phenylacetyl complexes, as well as the analogous trifluoroacetyl complex,^{2b} undergo the migration reaction in the solid state. This has made it possible to determine the enthalpy change, ΔH_T , at the reaction temperature, T , and at standard conditions, ΔH_0 .

The reaction studied is shown in eq 3. When the



orange solid, Ia-d, is heated to a temperature, T , which depends on the R group, the migration reaction occurs to give white compounds IIa-d. These were shown to be identical with the products formed in homogeneous solution by ir spectroscopy. The reaction was not complicated by weight loss and the exothermic peak for the migration reaction was well separated from the melting transition of the product. The enthalpy change for the reaction was determined at temperature T by standard differential calorimetric methods.^{3,4} These

(1) A. Wojcicki, *Advan. Organometal. Chem.*, **11**, 87 (1973).

(2) (a) M. Kubota, D. M. Blake, and S. A. Smith, *Inorg. Chem.*, **10**, 1430 (1971); (b) D. M. Blake, S. Shields, and L. Wyman, *ibid.*, **13**, 1595 (1974).

(3) A Perkin-Elmer Model DSC-1B differential scanning calorimeter was used in the study. Peak areas for the reaction were calibrated with respect to the heat of fusion of standard indium samples. A sapphire sample was used as a standard for the heat capacity determinations.

(4) (a) W. J. Smothers and Y. Chiang, "Handbook of Differential Thermal Analysis," Chemical Publishing Co., New York, 1966; (b) Instructions for Differential Scanning Calorimetry, Perkin-Elmer Corporation Publication No. 990-9556 (1966); (c) M. J. O'Neill, *Anal. Chem.*, **38**, 1331 (1966).