Reactions of Methylated Cyclopropanes and Olefins with Chloroplatinic Acid

II. Monoacylation and the Formation of β,γ-Unsaturated

Carbonyl Complexes of Platinum Dichloride

Steven E. Earnest and David B. Brown*

Department of Chemistry

University of Vermont

Burlington, Vermont 05401

Summary

Upon reaction with chloroplatinic acid in acid anhydride solvents, several methyl-substituted cyclopropanes and olefins form platinum dichloride adducts of β,γ-unsaturated carbonyls in which the ligand is bound to platinum through both the olefin π-system and a lone pair on the carbonyl oxygen. The cyclopropane reactions are shown to proceed via initial isomerization to an olefin, followed by acylation and proton loss. The stereochemistry of the products is shown to be dependent upon the substitution on the carbons α and β to the carbonyl, and in the case where both the α- and β-carbons are methyl-substituted a single conformation cf the product is isolated.

Introduction

Although the reaction of cyclopropane with chloroplatinic acid in
acetic anhydride provides a facile route to the platinocyclobutane moiety,
this same reaction using substituted cyclopropanes is much more complex.
As mentioned in the previous paper (1), at least five distinct complexes
may be derived from the reaction of 1,1-dimethylcyclopropane with chloro-
platinic acid--two isomeric pyrylium ions, a platinum complex of a β,γ-
unsaturated carbonyl, an olefin complex derived from isomerization of the
cyclopropane, and the genuine insertion product. In acid anhydride sol-
vents two processes predominate, the formation of pyrylium ion salts (1)
and the formation of β,γ-unsaturated carbonyl complexes of platinum di-
chloride, to be discussed here.

Complexes of this type are among the oldest organometallic compounds
known, the material derived from mesityl oxide, $PtCl_2(C_6H_{10}O)$, being
reported by Zeise in 1840 (2). However, the molecular structure of this
compound has only recently been determined. Using a combination of
physical and chemical techniques, Gillard, et al. (3) have shown that
this material is in fact derived from the isomerization product of mesityl
oxide, 4-methyl-pent-4-ene-2-one, and that this ligand can be removed in-
tact by reaction of the complex with triphenylphosphine. The net result
of this two-step process is the deconjugation of an α,β- to a β,γ-
unsaturated carbonyl. This is then an interesting example of a transfor-
mation in the reverse direction from that observed for the free ligand.

Under certain conditions, then, complexes of β,γ-unsaturated carbonyls
bound chelatively to platinum may be prepared by acylation of cyclopropanes.
Such complexes may also be formed from olefins, and our results with both
of these systems will be reported here.

Experimental Section

Materials and techniques used are in all cases the same as those detailed in the previous paper (1) and will not be repeated here.

Reaction of Chloroplatinic Acid with 1,1-Dimethylcyclopropane in Acetic Anhydride.

Chloroplatinic acid (0.69g, 1.3 mmole) was dissolved in acetic anhydride (25 ml) and allowed to react with 1,1-dimethylcyclopropane. The initial product was a mixture of pyrylium ions. Upon standing, more product was formed which, based on infrared measurements, was a mixture of pyrylium ion salts and the β,γ-unsaturated carbonyl complex. Upon refrigeration overnight, a yellow powder formed (50 mg, 0.132 mmole), which was subsequently shown to be the β,γ-unsaturated carbonyl complex, 2,3-dimethyl-1-pentene-4-one platinum dichloride, I.

Anal. Calcd. for $C_7H_{12}OPtCl_2$: C, 22.23; H, 3.20; Pt, 51.59; Cl, 18.75; mol. wt., 379. Found: C, 22.20; H, 3.44; Pt, 51.60; Cl, 18.50; mol. wt. (osmometrically in methanol), 376.

An identical product was obtained from the analogous reaction using either cis- or trans-1,2-dimethylcyclopropane, or a mixture of both isomers. I was the only product observed in the reaction with 2-methyl-2-butene.

Greater yields of these products could be obtained, but at the expense of purity. Crude product, as a mixture of pyrylium ions and I, was formed upon precipitation with ether. Although separation by fractional crystallization from methanol was successful in certain cases, it did not prove useful as a general synthetic route, both because of the relative insolubility of both types of products in most solvents and also because of the poor stability of the complex in solution at elevated temperatures.

Reaction of Chloroplatinic Acid with 1,1-Dimethylcyclopropane in Propanoic Anhydride.

Chloroplatinic acid reacted with 1,1-dimethylcyclopropane in propanoic anhydride to give 2,3-dimethyl-1-hexene-4-one platinum dichloride, II.

464

Anal. Calcd. for $C_8H_{14}OPtCl_2$: C, 24.50; H, 3.60; Pt, 49.74;

Cl, 18.08. Found: C, 25.08; H, 3.93; Pt, 49.20; Cl, 17.80.

II was also formed in the reaction using 1,2-dimethylcyclopropane, and as the sole product in the reaction with 2-methyl-2-butene.

Reaction of Chloroplatinic Acid with Trans-2-butene in Acetic Anhydride.
Trans-2-butene was bubbled through a cooled solution of chloroplatinic acid in acetic anhydride, forming 3-methyl-1-pentene-4-one platinum di-chloride, III, as the sole product.

Anal. Calcd. for $C_6H_{10}OPtCl_2$: C, 19.80; H, 2.77; Pt, 53.58;

Cl, 19.50. Found: C, 18.42; H, 3.16; Pt, 53.86; Cl, 19.41.

What appears to be the same product was formed in extremely low yield upon bubbling methylcyclopropane through a solution of chloroplatinic acid in acetic anhydride.

Reaction of Chloroplatinic Acid with Trans-2-butene in Propanoic Anhydride.
Trans-2-butene was bubbled through a cooled solution of chloroplatinic acid in propanoic anhydride, forming 3-methyl-1-hexene-4-one, IV, as the sole product.

Anal. Calcd. for $C_7H_{12}OPtCl_2$: C, 22.23; H, 3.20; Pt, 51.59;

Cl, 18.75. Found: C, 22.11; H, 3.42; Pt, 51.50; Cl, 18.65

Reaction of Chloroplatinic Acid with Isobutylene (2-methyl-1-propene) in
Propanoic Anhydride. Isobutylene was bubbled through a cooled solution of chloroplatinic acid in propanoic anhydride, forming 2-methyl-1-hexene-4-one platinum dichloride, V, in addition to the pyrylium ion salt.

Anal. Calcd. for $C_7H_{12}OPtCl_2$: C, 22.23; H, 3.20; Pt, 51.59;

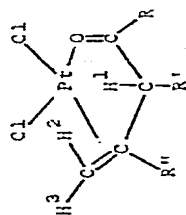Cl, 18.75. Found: C, 22.17; H, 3.50; Pt, 51.32; Cl, 18.76.

There was no evidence for the formation of any β,γ-unsaturated carbonyl complex from the analogous reaction in acetic anhydride.

Results

The reaction of alkylated cyclopropanes with chloroplatinic acid can lead to four different types of product—platinocyclobutanes (insertion complexes), olefin complexes, pyrylium ions salts, and β,γ-unsaturated carbonyl complexes. Fortunately, the presence of the latter two materials can be readily identified in a product, or mixture of products, using infrared measurements.

Several regions of the spectrum are distinctive for the β,γ-unsaturated carbonyl complexes. First, a weak but distinctive C-H absorption near 3080 cm^{-1} is present in these complexes and is characteristic of the vinyl group (4). The most important characteristic band, and one which most clearly distinguishes these complexes from the other possible products, is a strong absorption near 1585 cm^{-1}. This band, which is undoubtedly the carbon-oxygen stretching mode, is shifted ca. 100 cm^{-1} to lower frequency from observed values in the free ligands. This shift, which is characteristic (5-8) of oxygen-bonded ketones, provides the best evidence for coordination of the carbonyl group to platinum. Evidence for coordination of the olefin is also present in the form of weak absorptions near 1500 cm^{-1}. Finally, the platinum-chlorine stretching region is distinctive in that the two absorptions observed, at ca. 360 and 310 cm^{-1}, are higher than those generally found in square planar platinum complexes (9).

Solubility problems complicate nmr spectral investigations, since the complexes are at best only poorly soluble in solvents with which they do not react. As a consequence, no nmr data are available for some of the complexes prepared. Although the complexes react slowly with dimethyl-sulfoxide, they appear to be relatively stable in acetonitrile, so that spectra reported are generally for freshly prepared solutions in CD$_3$CN. In spite of these difficulties, the nmr spectra provide the most detailed

Table I. Spectral Data for β,γ-Unsaturated Ketone Complexes

Compound			NMR[a]					IR[b]		
R	R'	R''	R	R'	R''	H¹	H²,H³	ν_{CO}	$\nu_{C=C}$	ν_{Pt-Cl}
I CH_3	CH_3	CH_3	2.42	1.58(d) (J_{HH}=7.5)	2.42	3.50(q) (J_{HH}=7.5)	4.16,4.82 (J_{PtH}=70.5,64.5)	1583	1500	362,310
II C_2H_5	CH_3	CH_3	1.20(t) 2.87(q) (J_{HH}=6.3)	1.65(d) (J_{HH}=7.5)	2.13 (J_{PtH}=33)	3.72(q) (J_{HH}=7.5)	4.20,4.89 (J_{PtH}=72.0,63.0)	1583	1500	365,313
III CH_3	CH_3	H						1587	1500	360,312
IV[c] C_2H_5	CH_3	H	1.11(t) 2.65(q) (J=7.5) 1.02(t) 2.79(q) (J=7.5)	1.32(d) (J=7.0) 1.68(d) (J=7.0)	ca 3.5	ca 4.8		1585	1495	360,315
V C_2H_5	H	CH_3	1.05(t) 2.59(q) (J=8.0)	3.64[d]	1.88	--	4.68,4.77 (J_{PtH}=71.0,68.0)	1590	1492	358,309
CH_3	H	CH_3	2.41[e]	3.49[d]	1.80 (J_{PtH}=32)	--	4.16,4.70 (J_{PtH}=72,63)	1600[f]		367,325[g]

[a] Spectra in acetonitrile-d_3. Chemical shifts (δ) referred to TMS, δ = 0. Coupling constants in Hz.
[b] KBr pellets. Frequencies in cm⁻¹. [c] See text. [d] AB pattern. [e] Ref. 3. [f] Ref. 10. [g] Ref. 9.

probe to molecular structure. Combined with the analytical data, the
conductivity appropriate for a non-electrolyte, and the monomeric molecular
weight, the nmr data lead to the structural assignments given in Table I.

Discussion

The nmr spectral data clearly establish the presence of β,γ-unsaturated
carbonyl complexes. Although α,β-unsaturated carbonyls might be expected
to form more readily, particularly in reactions of the olefins, the presence
of the β,γ-unsaturated species is favored on steric grounds, and, of course,
has precedent in the case of mesityl oxide (3). Assuming coordination to
platinum through both the olefin and the carbonyl oxygen, the β,γ-unsatu-
rated carbonyl gives rise to the conformationally more stable $5\frac{1}{2}$-membered
ring. The added stability of the $5\frac{1}{2}$-membered ring has been established
through thermodynamic measurements in the case of silver complexes of both
unsaturated α-amino acids (11) and unsaturated derivatives of acetic and
iminodiacetic acids (12). The limited evidence available suggests that for
unsaturated carbonyl complexes of platinum the isomerization $\alpha,\beta \rightarrow \beta,\gamma$ is
facile (3) whereas the isomerization $\gamma,\delta \rightarrow \beta,\gamma$ is not (9). However, γ,δ
to β,γ isomerization was found to be competitive with hydrogenation using
a mixed chloroplatinic acid-stannous chloride catalyst in a hydrogen
atmosphere (13), and, in the case of 2-(alkenyl)pyridine derivatives of
$W(CO)_4$, isomerization in both directions is facile (14).

It is much more difficult to determine unambiguously the mode of
coordination of the carbonyl group, since it can conceivably coordinate
either through the π-orbitals as an olefin, or through the oxygen lone
pairs as a sigma donor. It is believed that several α,β-unsaturated
carbonyl complexes of iron (15), molybdenum (16) and tungsten (17) involve
bonding of the ligand as a π-hetero-1,3-diene, and in fact such bonding has
been confirmed crystallographically in at least one case (18). A greater

variety of examples exist where bonding is suggested to occur through the oxygen lone pair, and although this has not been confirmed for simple unsaturated carbonyl complexes, bonding through the oxygen lone pair has been demonstrated crystallographically for manganese (19), ruthenium (20), and palladium (21) complexes. Since bonding through the lone pair seems compatible with the expected behavior for simple platinum complexes of this sort, we have assumed such bonding throughout, although crystallographic confirmation would be desirable. Some support for this assumption may be derivable from the stereochemical preferences exhibited by these complexes (vide infra).

The mode of formation of these complexes, particularly starting from the cyclopropanes, is not obvious. As discussed in the previous paper, an intermediate in the formation of pyrylium ions from cyclopropanes must be a β,γ-unsaturated carbonyl. However, for both 1,1-dimethylcyclopropane and 1,2-dimethylcyclopropane the β,γ-unsaturated carbonyl complexes formed are not those demonstrated to be necessary intermediates in the formation of pyrylium ions. Thus it is clear that the formation of (β,γ-unsaturated carbonyl)PtCl$_2$ complexes does not arise from trapping of intermediates in a more general reaction, a fact consistent with the observation that such complexes generally precipitate from solution after the pyrylium ions have been isolated. This, of course, does not rule out reaction by a parallel pathway equivalent in that it involves conventional carbonium ion intermediates. Nonetheless, such a path is unlikely, since for 1,1-dimethylcyclopropane rearrangement to the carbonium ion necessary for formation of the observed β,γ-unsaturated carbonyl would require four distinct steps, including one which places the positive change adjacent to the carbonyl.

There is only limited precedent for acylation of cyclopropanes, but the results observed here for reactions involving H$_2$PtCl$_6$ are consistent with the reported reaction (22) of 1,1-dimethylcyclopropane with acyl

chloride and aluminum chloride. In that case the only products observed
were 4-chloro-3,4-dimethylpentane-2-one and 3,4-dimethyl-pent-3-ene-2-one,
which may be derived from the same carbonium ion intermediate, VI, by either
chloride addition or proton loss (Figure I). This same intermediate can
easily account for the products observed in the reaction with the platinum
complex, as proton loss to form the β,γ-unsaturated carbonyl should be
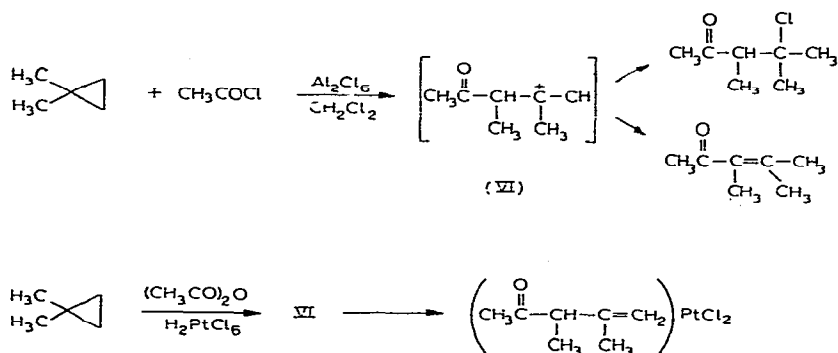facile in the presence of platinum chloride (3).

Figure 1. Acylation of 1,1-dimethylcyclopropane.

Hart and Schlosberg (22) conclude that the carbonium ion VI is derived
by acylation of the olefin derived from isomerization of 1,1-dimethylcyclo-
propane, and our data is consistent with a similar pathway (Figure 2). We
offer the following supportive evidence. First, under similar conditions
the olefin which would be formed, 2-methyl-2-butene, reacts readily to form
the same β,γ-unsaturated carbonyl complex, I. Second, the observation that
the β,γ-unsaturated carbonyl complex is formed subsequent to pyrylium ion
formation suggests that it proceeds by a unique path. Since all other routes
to the product involve acylation of the cyclopropane itself (as is required
for pyrylium ion formation) they might be expected to proceed at comparable rates.
Finally, under slightly modified conditions the isomerization to an olefin has
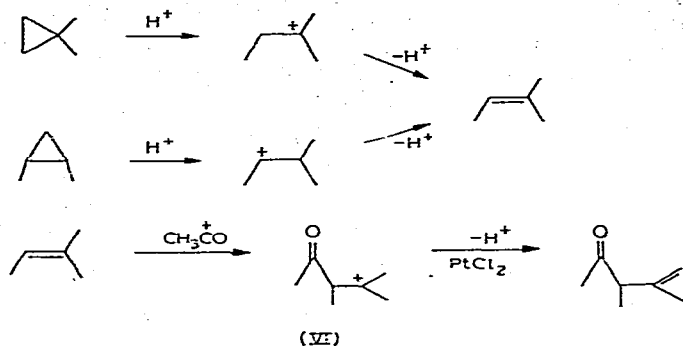
(VI)

Figure 2. Proposed mechanisms for the formation of (β,γ-unsaturated carbonyl) platinumdichloride complexes from 1,1-dimethyl-cyclopropane and 1,2-dimethylcyclopropane.

been observed. Specifically, the reaction between 1,1-dimethylcyclopropane and chloroplatinic acid in acetic acid leads to the formation of the platinum complex of 2-methyl-2-butene, $[PtCl_2(C_5H_{10})]_2$. Furthermore, the reaction of chloroplatinic acid, acetyl chloride, and 1,1-dimethylcyclopropane in acetic acid (where isomerization to the olefin is a known reaction) produces only the β,γ-unsaturated carbonyl complex. By contrast, the same reactants in ethyl acetate (where insertion is a known reaction) produce only a pyrylium ion salt (I).

An alternative mechanistic route involves acylation of the ring and transformation to an edge-protonated cyclopropane. Rearrangement of such a species and bond cleavage could ultimately lead to the appropriate carbonium ion, VI, but several of the steps involved would appear to require a very high activation energy. Hart and Schlosberg (22) ruled out such a mechanism in their studies of the aluminum chloride catalyzed reaction of 1,1-dimethyl-cyclopropane, and for similar reasons we consider reactions involving edge-protonated cyclopropanes to be unlikely in the reactions involving chloroplatinic acid.

The results of the reactions involving 1,2-dimethylcyclopropane are con-

sistent with the postulated mechanism. Acid-catalyzed isomerization to 2-
methyl-2-butene (Figure 2), followed by acylation and proton loss, leads
directly to the observed product. Routes involving direct acylation of the
cyclopropane ring are again less likely. Acyl attack would be expected to
occur at C_3, with cleavage of the C_1-C_3 bond, and this reaction cannot lead
to the observed product.

Methylcyclopropane would be expected to rearrange to a mixture of cis-
and trans-2-butenes. Since trans-2-butene reacts in acetic anhydride to form
III, an identical product is expected from methylcyclopropane. Although not
isolated in sufficient quantities or purity for thorough characterization, the
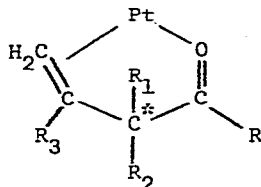available data does support the formation of III in this reaction.

The failure to isolate similar products from other cyclopropanes is
somewhat surprising. Neither 1,1,2-trimethylcyclopropane nor 1,1,2,2-tetra-
methylcyclopropane reacts to form unsaturated carbonyl complexes in either
solvent. It is likely that the high degree of substitution which would be
present in the olefin isomerization products would effectively hinder formation
of a platinum complex. This in turn would eliminate the possibility of form-
ing the β,γ-unsaturated carbonyl complexes, since it is likely that acylation
occurs on the platinum-bound olefin. Acylation independent of platinum would
lead to α,β-unsaturation. Although subsequent isomerization is possible,
direct formation of the β,γ-unsaturated complex on platinum seems more likely,
particularly since platinum is undoubtedly involved in the isomerization step.
This hypothesis derives its most substantial support from the failure of
mesityl oxide to form a β,γ-unsaturated carbonyl complex under the standard
reaction conditions. This confirms that α,β-unsaturated carbonyls formed in
bulk solution are not reactive toward complex formation.

Although complexes of β,γ-unsaturated carbonyls can be formed from the
reactions of cyclopropanes, their formation from olefins is much more facile,
as might be expected from the mechanism proposed for the cyclopropanes. Under

the appropriate conditions isobutylene, 2-methyl-2-butene, and trans-2-butene

may all be acylated to form the β,γ-unsaturated carbonyl complexes. The products

formed are, in each case, those expected from acyl attack on the least substi-

tuted carbon of the double bond, followed by proton loss to form the β,γ-un-

saturated system. As discussed in the previous paper, complexes of this type

are not formed from the reactions of 2-methyl-1-butene or 2-ethyl-1-butene,

the only products observed being pyrylium ions. The complete lack of reac-

tivity for cis-2-butene is somewhat surprising. However, metal complexes with

cis-olefins are known to be more stable than their trans analogs (23), and if

the platinum complex formed with cis-2-butene is sufficiently stable, the initial

acylation may be inhibited

Product Stereochemistry

These complexes provide a variety of unique stereochemical possibilities.

Using the numbering scheme below, three distinct types of stereochemical

behavior are observed. In the free ligand when $R_1 = R_2 = H$,

$$
\begin{array}{c}
\text{Pt} \\
H_2C \diagdown \diagup \diagdown O \\
\diagdown C \diagdown \ \ \diagup C \diagup \\
R_3 \ \ \ \ C^* \ \ \ R \\
R_1 \\
R_2
\end{array}
$$

center C^* is prochiral, and R_1 and R_2 would give rise to a single nmr absorp-

tion. In the complex, however, centers R_1 and R_2 become anisochronous (24),

leading to the observed AB absorption pattern. When R_1 is not equivalent to

R_2, then center C^* becomes chiral, and the free ligand is expected to exist

as the racemic mixture of enantiomers. The conformational rigidity of the

complex induces a second level of asymmetry, and each enantiomer leads to a

diastereomeric pair (25) of complexes which are distinguishable by nmr. The

net result is the formation of four complexes--two diastereomeric racemic mix-
tures. Examination of models suggests that in the most plausible conformation
the substituents on C^* are best described as being either equatorial (R_1) or
axial (R_2) with respect to the plane defined by $PtCl_2$. For complex IV ($R_3 =$
H; R_1, R_2 = H, CH_3) the observed nmr spectrum corresponds to the superposition
of two comparable, but not equivalent, spectra corresponding to the diastereo-
mers having the methyl group either axial or equatorial. Similar behavior
might be expected for I and II (R_3 = CH_3; R_1, R_2 = H, CH_3; R = CH_3, C_2H_5),
but it is not found, the nmr corresponding to a single species. We ascribe this
result to a conformational preference which leads to a single diastereomer.
Substituent R_3 is always axial with respect to the $PtCl_2$ plane. If the diastereo-
mer with R_2 = CH_3 were formed, the methyl groups R_2 and R_3 would be in an
eclipsed configuration. Clearly, the conformation with R_2 = H would be favored,
and our nmr data suggests that it is indeed the only one formed (26). Since
complex III differs from IV only in substitution remote from the coordination
sites (III, R = CH_3 vs. IV, R = C_2H_5) similar behavior might be expected. Un-
fortunately, the solubility of III is such that nmr spectra could be obtained
only in dimethylsulfoxide. Although these spectra are of poor quality, and are
complicated by the presence of decomposition products, they appear to be the
result of overlapping spectra, and thus suggest the presence of both for this
compound as well as for compound IV.

This work has demonstrated that in the presence of platinum complexes,
certain olefins and cyclopropanes may be acylated by a route which differs
significantly from that followed using typical Lewis acid catalysts, in that
platinum complexes of β,γ-unsaturated carbonyls are formed. Since the β,γ-un-
saturated carbonyls may be released from the complex upon reaction with phos-
phines, these reactions have potential synthetic utility. Investigations are
are in progress to determine the generality of these reactions and to devise
improved synthetic routes.

References

1. S. E. Earnest and D. B. Brown, previous paper.

2. H. Zeise, *J. Prakt. Chem.* 20, 193 (1840).

3. R. D. Gillard, B. T. Heaton, and M. F. Pilbrow, *J. Chem. Soc.* (A), 353 (1970).

4. L. J. Bellamy, The Infrared Spectra of Complex Molecules, 3rd Edit.; Halsted Press, New York (1975).

5. D. M. Roe, C. Caluo, N. Krishnamachari, and P. M. Maitlis, *J. Chem. Soc. Dalton*, 125 (1975).

6. C. P. Casey and C. A. Bunnell, *Inorg. Chem.* 14, 796 (1975).

7. Y. Nakamura and K. Nakamoto, *Inorg. Chem.* 14, 63 (1975).

8. A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. Dalton*, 1848 (1973).

9. B. T. Heaton and D. J. A. McCaffrey, *J. Organometal. Chem.* 43, 437 (1972).

10. G. W. Parshall and G. Wilkinson, *Inorg. Chem.* 1, 896 (1962).

11. M. Israeli and L. D. Pettit, *J. Inorg. Nucl. Chem.* 37, 999 (1975).

12. M. Israeli and L. D. Pettit, *J. Chem. Soc. Dalton*, 414 (1975).

13. N. V. Borunova, L. Kh. Freidlin, and Ya. G. Mukhtarov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 849 (1974).

14. B. T. Heaton and D. J. A. McCaffrey, *J. Organometal. Chem.* 66, C46 (1974).

15. G. Cardaci, *J. Am. Chem. Soc.* 97, 1412 (1975).

16. D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.* 4, 1323 (1965).

17. R. B. King and A. Fronzaglia, *Chem. Comm.*, 274 (1966).

18. A. DeCian and R. Weiss, *Acta Cryst.* 28B, 3273 (1972).

19. J. R. Blickensderfer, C. B. Knobler, and H. D. Kaesz, _J. Am. Chem. Soc._ **97**, 2686 (1975).

20. A. J. P. Domingos, B. F. G. Johnson, J. Lewis, and G. M. Sheldrick, _Chem. Comm._, 912 (1973).

21. W. M. Roe, C. Calvo, N. Krishnamachari, K. Moseley, and P. M. Maitlis, _J. Chem. Soc._, _Chem. Comm._, 436 (1973).

22. H. Hart and R. H. Schlosberg, _J. Am. Chem. Soc._ **90**, 5189 (1968).

23. M. A. Muhs and F. T. Weiss, _J. Am. Chem. Soc._, **84**, 4697 (1962).

24. W. B. Jennings, _Chem. Rev._ **75**, 307 (1975).

25. K. Mislow and M. Raban, _Topics in Stereochem._, N. L. Allinger and E. L. Eliel, eds., **1**, 1 (1967).

26. The free energy difference between the two eclipsed forms of butane is about 2.5 kcal/mole (27), and this value may then be taken as a reasonable estimate for the energy difference in the two forms where the methyl group is axial or equatorial. Such a free energy difference leads to the expectation that at equilibrium less than 2% of the axial conformer should be present.

27. R. F. Brown, _Organic Chemistry_, Wadsworth Publishing Co., Inc., Belmont, Cal. (1975), p. 121.