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# Carbon-13 Nuclear Magnetic Resonance Spectroscopy in the Study of Conformational Effects among Cyclohexyl Phosphorus Compounds

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$^{13}$C NMR spectra were obtained for the cis and trans isomers resulting from situating each of the following functions at the 4 position of *tert*-butylcyclohexane: $PH_2$, $PMe_2$, $PCl_2$, $P(OMe)_2$, $PSMe_2$, $^{+}PMe_3I^{-}$. For the trans isomers, the $^{13}$C spectra were consistent with diequatorial substitution. In the cis isomers, the trivalent functions occupied the normal axial position but the larger $PSMe_2$ and $^{+}PMe_3$ groups, as seen from chemical shift effects, caused considerable distortion of the ring, either through flattening about the 1,4-ring carbons or by adoption of a twist conformation. C–P coupling constants favor the former explanation. When $PSMe_2$ and $^{+}PMe_3$ are placed in the cis 4 position of methylcyclohexane, the $^{13}$C NMR evidence suggests that they adopt the equatorial position and force methyl into the axial position. A minimum *A* value for these phosphorus functions derived from this information is 3.0 kcal/mol. The $PMe_2$ group has an *A* value similar to that for methyl, and the $^{13}$C NMR spectrum for the 1,4 cis isomer is consistent with an approximately 1:1 mixture of equilibrating conformers. Among the trivalent functions, the three-bond $^{13}$C–$^{31}$P coupling constant was found to be under strong steric control for the primary phosphines alone; the other functions showed only a small difference in $^{3}J_{PC}$ between the cis and trans isomers. The spectra of 24 cyclohexane derivatives were recorded during this study and interpreted by existing generalities.

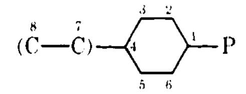
$^{13}$C NMR spectroscopy is firmly established as a technique providing valuable information about conformational aspects of six-membered rings.[2,3a] We have now applied it in a systematic way to cyclohexanes containing various phosphorus functions and report our results in this paper.[4] We have done this first to test the validity of our *A* values for some trivalent functions, which we have recently determined by $^{31}$P NMR spectroscopy,[5] and then to obtain qualitative information on some tetravalent phosphorus functions, which could not be determined by the $^{31}$P approach used. Since the trivalent groups studied [$PH_2$, $PCl_2$, $PMe_2$, and $P(OMe)_2$] all had sizable *A* values (±0.2 kcal/mol of that for methyl,[7] 1.7), it might be expected that tetravalent functions would show even larger values, indeed possibly approaching that of *tert*-butyl. A precise value for this group is still lacking but the range 4–5 kcal/mol has been proposed.[7,8]

**$^{13}$C Spectral Data and Assignments.** All data for the 24 compounds studied are recorded in Table I. For measurements on cis, trans isomers (whose structures have been determined in previous work[5]), data were obtained on samples enriched in the pertinent form, in some cases as high as 95%. Assignments are easily made on the following lines: (1) C-1 and C-4 are of half the intensity of C-2,6 and C-3,5. C-1 is always a doublet through coupling to $^{31}$P; C-4 shows no coupling. (2) Methyls on phosphorus are always the most upfield doublets. (3) Methyls on C-4 are the most shielded of the uncoupled carbons, and are of unit intensity. (4) *tert*-Butyl carbons are recognized from their intensities (weak quaternary signal, strong methyl signal) and near identity of position in both cis and trans forms. (5) Differentiation between C-2,6 and C-3,5 was based on a combination of shift and P–C coupling effects. For $PH_2$, the differentiation is easy; C-2,6 are well downfield (δ 36.0) of C-3,5 (27.4) since the former carbons feel a strong β effect due to phosphorus, while the latter carbons are not greatly shifted from the cyclohexane value (27.7). The same effect is seen for $NH_2$[9] (δ $C_{2,6}$ 37.7; δ $C_{3,5}$ 25.8). For all other phosphorus functions, the atoms replacing hydrogen can be expected to exert an additional upfield γ effect at C-2,6, compensating in part for the β effect acting in the opposite direction. As a result signals for C-2,6 move closer to those for C-3,5, as is true in many cyclohexyl derivatives.[9] We have reported on the same effect in noncyclic phosphorus derivatives.[10] To distinguish between these carbons, P–C coupling constants were used. Among the noncyclic trivalent derivatives, $^{2}J$ is larger than $^{3}J$, and the values found for the cyclohexyl derivatives were very similar to those seen for *n*-butyl derivatives.[10] For the tetravalent functions, $^{3}J$ is considerably larger than $^{2}J$ in the *n*-butyl series,[10] and comparable values were obtained for the cyclohexyl derivatives.

For derivatives bearing trans 4-alkyl substituents, assignments were straightforward; shift effects occurred that resembled closely those seen on placing the same alkyl group on cyclohexane. For the cis derivatives, additional effects are present owing to the placement of one group in the axial position; these effects are more appropriately discussed in later sections of this paper.

**Effects of Phosphorus Functions on the Carbon Signals of Cyclohexane.** It is known from our previous studies based on $^{31}$P NMR spectroscopy[5] that the six phosphorus functions are of considerable size (*A* > 1.5 kcal/mol) and will occupy the equatorial position on cyclohexane to a very large extent. Therefore, spectra for monosubstituted cyclohexanes can be taken as arising from the equatorial conformers. The shifts caused by these equatorial phosphorus substituents on the cyclohexane carbons are summarized in Table II in terms of α, β, γ, and δ effects at C-1, C-2,6, C-3,5, and C-4, respectively.

Table I.[a] $^{13}$C NMR Spectral Data



| Compd | Identity of 4 substituent | C-1 | C-2,6 | C-3,5 | C-4 | P–CH$_3$ | C-7 | C-8 |
|---|---|---|---|---|---|---|---|---|
| A. Primary Phosphines ($P = PH_2$)[b] | | | | | | | | |
| 1 | H | 27.2 (6) | 36.0 (7) | 27.4 (8) | 25.9 | | | |
| 2 | *trans-t*-Bu | 27.2 (7) | 36.6 (7) | 28.5 (9) | 47.3 | | 32.2 | 27.6 |
| 3 | *cis-t*-Bu | 23.5 (9) | 32.7 (8) | 21.8 (2) | 48.5 | | 32.4 | 27.5 |
| B. Tertiary Phosphines ($P = PMe_2$)[c] | | | | | | | | |
| 4 | H | 39.3 (8) | 28.9 (14) | 27.0 (10) | 26.0 | 11.3 (15) | | |
| 5 | *trans*-Me | 39.2 (7) | 29.1 (14) | 36.1 (11) | 32.2 | 11.6 (17) | 23.1 | |
| 6 | *trans-t*-Bu | 39.3 (9) | 29.4 (14) | 28.0 (11) | 48.0 | 11.5 (15) | 32.5 | 27.6 |
| 7 | *cis*-Me | 40.0 (9) | 25.6 (12) | 32.0 (8) | 30.4 | 12.4 (15) | 20.3 | |
| 8 | *cis-t*-Bu | 40.0 (10) | 28.9 (11) | 23.5 (8) | 49.0 | 13.1 (15) | 32.8 | 27.7 |
| C. Phosphonous Dichlorides ($P = PCl_2$)[b] | | | | | | | | |
| 9 | H | 48.5 (45) | 25.6 (16) | 26.0 (11) | 25.8 | | | |
| 10 | *trans-t*-Bu | 48.4 (45) | 26.0 (16) | 27.1 (11) | 47.4 | | 32.2 | 27.4 |
| 11 | *cis-t*-Bu | 49.3 (44) | 27.3 (15) | 23.8 (9) | 48.4 | | 32.6 | 27.6 |
| D. Dimethyl Phosphonites ($P = P(OMe)_2$)[b] | | | | | | | | |
| 12 | H | 41.3 (15) | 25.6 (17) | 26.7 (11) | 26.9 | [54.0 (14)][d] | | |
| 13 | *trans-t*-Bu | 41.0 (14) | 25.9 (17) | 27.4 (9) | 48.1 | [53.9 (13)][d] | 32.6 | 27.7 |
| 14 | *cis-t*-Bu | 38.2 (18) | 26.7 (14) | 24.5 (7) | 48.8 | [53.8 (13)][d] | 32.7 | 27.7 |
| E. Phosphine Sulfides ($P = PSMe_2$)[c] | | | | | | | | |
| 15 | H | 41.1 (54) | 25.6 (3) | 26.2 (14) | 25.7 | 18.5 (52) | | |
| 16 | *trans*-Me | 40.7 (54) | 25.7 (~2) | 34.8 (15) | 32.1 | 18.6 (55) | 22.6 | |
| 17 | *trans-t*-Bu | 41.2 (53) | 26.4 (3) | 27.3 (13) | 47.5 | 18.6 (52) | 32.6 | 27.6 |
| 18 | *cis*-Me | 41.0 (54) | 19.8 (~2) | 31.5 (14) | 26.6 | 18.6 (55) | 17.4 | |
| 19 | *cis-t*-Bu | 36.7 (51) | 24.9 (2) | 23.2 (4) | 46.0 | 21.0 (53) | 32.7 | 27.5 |
| F. Phosphonium Iodides ($P = {}^+PMe_3I^-$)[c] | | | | | | | | |
| 20 | H | 32.0 (52) | 25.1[e] | 25.5 (15)[e] | 25.1[e] | 7.5 (52) | | |
| 21 | *trans*-Me | 31.7 (51) | 25.2 (~2) | 34.0 (14) | 31.6 | 7.6 (53) | 22.5 | |
| 22 | *trans-t*-Bu | 32.1 (51) | 25.8 (3) | 26.5 (15) | 47.2 | 7.8 (55) | 32.6 | 27.6 |
| 23 | *cis*-Me | 32.0 (52) | 19.7 (~2) | 30.9 (13) | 26.2 | 7.6 (53) | 17.5 | |
| 24 | *cis-t*-Bu | 29.2 (48) | 24.2 (2) | 23.8 (4) | 45.6 | 10.0 (52) | 32.7 | 27.4 |

[a] Chemical shifts in parts per million downfield from internal $Me_4Si$. Values in parentheses are P–C coupling constants (Hz), where observed. [b] Neat samples. [c] $CDCl_3$ solutions. [d] Values for $CH_3$–O. [e] Severe peak overlap did not allow accurate determination of coupling constants.

Table II. Chemical Shift Effects on the Cyclohexane Ring by Equatorial P Substituents[a]

| | α | β | γ | δ |
|---|---|---|---|---|
| $PH_2$ | −0.5 | +8.3 | −0.3 | −1.8 |
| $PMe_2$ | +11.6 | +1.2 | −0.7 | −1.7 |
| $PCl_2$ | +20.8 | −2.1 | −1.7 | −1.9 |
| $P(OMe)_2$ | +13.6 | −2.1 | −1.0 | −0.8 |
| $PSMe_2$ | +13.4 | −2.1 | −1.5 | −2.0 |
| $^+PMe_3$ | +4.3 | −2.6 | −2.2 | −2.6 |

[a] Negative signs refer to shielding, positive to deshielding, of the carbons of cyclohexane (δ 27.7) on replacement of H by the P function.

Of the various substituents, all but $PH_2$ and $^+PMe_3$ have been studied previously with regard to their effects on the carbons of *n*-butane.[10] In general, effects on cyclohexane are similar in kind.

In our previous work on noncyclic compounds,[10] it was found that $PMe_2$, $PCl_2$, $P(OMe)_2$, and $PSMe_2$ groups exert large, quite different deshielding effects on α carbons, but have negligible effects on β carbons owing to the compensating shielding γ effect by the atoms attached directly to the phosphorus. On examining data for the cyclohexyl compounds, the same effects are apparent at the α and β positions. The $^+PMe_3$ group falls in the same category, although it has, as expected,[11] a significantly smaller α effect than do the other groups. The $PH_2$ group causes shielding of the carbon of methylphosphine by 2.3 ppm relative to methane, presumably through its electron-releasing inductive effect relative to carbon.[3b] In the cyclohexyl derivative, its α effect is negligible. The deshielding β effect is substantial; indeed it is the largest β effect (8.3 ppm) of any phosphorus group so far examined, with a magnitude comparable to that[2] for $-CH_3$ (8.4), $NH_2$ (10.1), and OH (8.4). The small α value for $PH_2$ relative to $PMe_2$ is easily explained by the presence in the latter of deshielding β effects by the methyl groups.

γ effects (shielding) felt at C-3,5 of the cyclohexane ring are quite small, but detectable, and indeed are of very similar magnitude to γ effects seen on C-3 of *n*-butyl chains.[10] (As will be noted later, larger γ effects are found in derivatives where the phosphorus group is in the axial position, where steric involvement with C-3,5 is pronounced.)

At C-4 of the cyclohexane ring, all six phosphorus functions cause a small (1–3 ppm) upfield shift. This δ effect is quite characteristic of a number of common substituents.[9] The opposite effect occurs in noncyclic compounds where the δ effect is weakly deshielding.[2,12] As observed by others,[13] the δ effect in the cyclohexanes does not correlate well with substituent polarity or size; the δ effect for $PH_2$ (1.8 ppm) is as large as that for $PMe_2$ (1.7) and larger than that (0.8) for the more polar $P(OMe)_2$ group. However, the tetravalent functions have relatively large $\delta$ effects ($PSMe_2$, 2.0; $^+PMe_3$, 2.6).

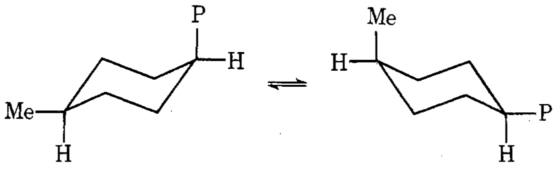
**$^{13}$C Spectra of *trans*-4-Alkylcyclohexyl Phosphorus Compounds.** When methyl or *tert*-butyl are substituted for hydrogen at the 4 position of the cyclohexyl phosphorus compounds, no significant changes in $^{13}$C shifts for C-1 occur. To illustrate, in the $PMe_2$ series values for C-1 are 39.3 (**4**, 4-H), 39.2 (**5**, 4-Me), and 39.3 (**6**, 4-*t*-Bu); similar data are found in Table II for the other functions. It is also noticed that methyls on phosphorus, where present, have chemical shifts independent of 4 substituents (e.g., for **4**, 11.3; **5**, 11.6; **6**, 11.5). These observations are consistent with a conformation for all compounds where the P substituent is predominantly in the equatorial position, for any significant amount of axial conformer would have led to noticeable $^{13}$C changes. These changes are seen on comparison of the trans isomers with the cis isomers, discussed in the next section.

Eliel et al.[13] have recently pointed out the operation of a shielding effect at $\gamma$ carbons by substituents held rigidly in the anti-periplanar relation. In cyclohexanes, the effect is felt at C-3,5 by substituents in the equatorial position. Our series of 4-*tert*-butyl compounds allows an extension of Eliel's considerations to anti-periplanar phosphorus substituents. We would expect from Eliel's generalizations that the effect will be quite small, for data so far available suggest the effect to be stronger for substituents based on second-row than for third-row elements. This is indeed what we observe. The $\gamma_{\text{anti-periplanar}}$ shielding constants for the phosphorus functions, derived from the data of Table II by comparing shifts for C-3,5 to that for the same carbons in *tert*-butylcyclohexane ($\delta$ 28.0), are as follows (where − is shielding, + is deshielding): $PH_2$, +0.5; $PMe_2$, 0.0; $PCl_2$, −0.9; $P(OMe)_2$, −0.6; $PSMe_2$, −0.7; $^+PMe_3$, −1.5. Only the last value approaches the size normally seen for second-row substituents[13] ($NH_2$, −1.6; others are in the range −1.6 to −2.7); the others are significantly smaller, and the $PH_2$ group even appears to exert a small $\gamma_{\text{anti-periplanar}}$ *deshielding* effect.

**$^{13}$C Spectra of *cis*-4-Alkylcyclohexyl Derivatives. With Trivalent Phosphorus Functions.** The *A* values for the trivalent phosphorus functions as determined by $^{31}$P NMR spectroscopy[5] are considerably smaller than that for *tert*-butyl (4–5 kcal/mol), and consequently these functions are forced into the axial position by a cis 4-*tert*-butyl group. The $^{13}$C spectra are convincing as proof of this statement, especially through the pronounced upfield shift at C-3,5 seen on comparing cis to trans. These gauche $\gamma$ shifts vary with the function, but are in the range (3–7 ppm) in which are found most common organic groups.[2,14] The magnitude of this type of $\gamma$ shift does not correlate well with group size or *A* value,[14] and it is not surprising to find $PH_2$ with the greatest gauche $\gamma$ effect (6.7). The steric differences in axial vs. equatorial conformers are also known to have influence on C-1 chemical shifts, but not always in predictable ways.[14] The phosphorus functions show this uncertainty; no correlation with either size or direction of the shifts seems to exist. This is seen to be true also for C-2,6. At C-4, however, the axial groups are consistently associated with downfield shifts (0.7–1.2 ppm) relative to the equatorial groups. Finally, it is noted that the methyls of $PMe_2$ are more deshielded (1.6 ppm) when in the axial conformation. Crowding of axial $PMe_2$ with C-3,5 therefore can be said to produce a downfield effect at methyl; this constitutes another[15] exception to the generality that crowding causes upfield shifts.

The availability of derivatives of trivalent phosphorus functions with fixed geometry provides an opportunity for the first consideration in this oxidation state of the dependence on dihedral angles of $^{13}$C–$^{31}$P coupling constants ($^3J_{PC}$) in the fragment PCCC.[16] For tetravalent functions, the steric influence on $^3J_{PC}$ is quite pronounced and appears to follow a Karplus-type relation.[17] In the cyclohexane system, larger coupling would be expected for trans isomers (dihedral angle about 180°) than for cis isomers (dihedral angle about 60°), and, as will be discussed in a later section, this is exactly what we have observed for the tetravalent functions $PSMe_2$ and $^+PMe_3$. However, only one of the four trivalent functions displayed this property; for $PH_2$, $^3J_{PC}$ of the trans isomer was 9 Hz, but only 2 Hz for the cis isomer. For the other functions, the values were quite similar, although for each the trans value was slightly the larger ($PMe_2$ trans 11, cis 8 Hz; $PCl_2$ trans 11, cis 9 Hz; $P(OMe)_2$ trans 9, cis 7 Hz). This result is quite surprising, pointing as it does to a role for the structure about the phosphorus atom in determining the magnitude of the steric control on $^3J_{PC}$. However, another case can be cited where a role for the oxidation state of phosphorus is seen. In a noncyclic system an increase in the number of carbons that can occupy gauche positions relative to phosphorus as bond rotation occurs necessarily decreases the averaged value for the dihedral angle derivable from the various conformations. If a Karplus-like relation prevails, then $^3J_{PC}$ should be smaller for the branched-chain compound. This is indeed observed[10] on comparing tri-*n*-butylphosphine sulfide ($^3J_{PC}$ = 16 Hz) to triisobutylphosphine sulfide ($^3J_{PC}$ = 9 Hz). It is *not* observed[10] on comparing tri-*n*-butylphosphine ($^3J_{PC}$ = 10 Hz) to triisobutylphosphine ($^3J_{PC}$ = 10 Hz). On the other hand, $^3J_{PC}$ in tertiary phosphines where phosphorus is conformationally constrained in a six-membered ring[18] (hence with dihedral angle about 60°) is quite small (2–3 Hz), and not at all consistent with the value observed here (8 Hz) for the freely rotating $PMe_2$ group with a similar dihedral angle (**8**). Further experimental exploration of this structure-dependent three-bond coupling phenomenon is called for.

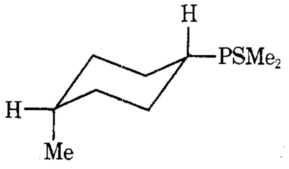
When methyl is present as the 4 substituent on the cyclohexane ring, it would be expected that the conformational equilibria would have nearly equal amounts of conformers I and II, since methyl and the trivalent phosphorus functions have rather similar *A* values. The $^{13}$C shifts should therefore be averaged for the values of each conformation, as was found to be true for $^{31}$P shifts.[5] To test for this effect, the spectrum of the cis $PMe_2$ derivative (**7**) was compared with that of the trans (**5**) where both substituents are equatorially disposed. The 4-methyl signal provides the clearest indication of the existence of the equilibrium in the cis isomer, for methyl is known to have a chemical shift when equatorial on the cyclohexane ring (23.5 ppm) that is quite different from that when axial (17.6 ppm).[19] These values are not influenced significantly by the presence of a 4 substituent.[19b,20] The value for trans isomer (**5**) is of the expected magnitude ($\delta$ 23.1) for equatorial disposition, but that for the cis isomer (**7**) ($\delta$ 20.3) is between the extremes, as would be expected for the proposed[5] equilibrium with $K \sim 1$. A similar effect is present for methyls of $Me_2P$; the deshielding (0.8 ppm) of these carbons in the cis isomer (**7**) relative to the trans (**5**) is half of that when this group is purely axial as in the cis 4-*tert*-butyl compound **8** (1.6 ppm downfield of trans **6**). Effects are also noticed at C-2,6 as well as C-3,5; substantial upfield shifts occur in the cis isomer since both types of carbons feel increased crowding with axial 4-$CH_3$ and $PMe_2$, respectively.



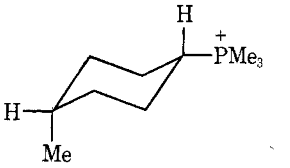
I II

**Tetravalent Phosphorus Functions.** The presence of the larger tetravalent phosphorus functions ($^+PMe_3$ and $PSMe_2$)

makes a profound difference on the $^{13}C$ spectra of 4-methylcyclohexyl derivatives. As had been earlier indicated by our $^{31}P$ NMR spectra,[5] these groups must have *A* values well in excess of that for $CH_3$ (1.7 kcal/mol) for the spectra give the expected indications of 4-$CH_3$ being forced into the axial position. Thus, the 4-$CH_3$ in the cis isomer of the sulfide (**18**) is 5.2 ppm upfield of that in the trans (**16**); for the phosphonium salt, the difference is 5.0 ppm (**23** vs. **21**). These values leave no doubt that the methyl is very largely in the axial position (cf. 5.9-ppm difference for axial and equatorial methyl in *cis*-1,4-dimethylcyclohexane at 180 K).[19b] Changes of similar magnitude are expected also at C-4, and are observed (sulfide 5.5, salt 5.4 ppm). Other spectral changes [upfield shifts at C-2,6 and C-3,5 and similarity of the sterically dependent (vide infra) values for $^3J_{PC}$] are also entirely consistent with the assignment of structures **25** and **26** as best representing the conformation of these phosphorus compounds. Although spectral evidence does not define the contribution of the minor conformer with equatorial methyl–axial P function, an estimate that 10% is present seems reasonable and leads to an equilibrium constant ($ax_P \rightleftharpoons eq_P$) of 9, and a free energy difference of $-1.3$ kcal/mol. By the principle of additivity,[21] extracting the $\Delta G°$ value for $CH_3$ of $-1.7$ kcal/mol leads to an *A* value ($-\Delta G°$) of 3.0 kcal/mol for the two phosphorus functions. We therefore propose this as a minimum *A* value which is consistent with the data so far available; the value could, of course, be significantly larger.

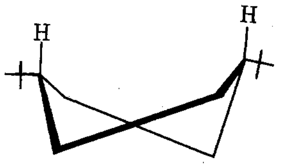


**25**



**26**

The *A* values for the tetravalent phosphorus functions therefore stand among the largest yet reported for a nonalkyl or nonaryl substituent.[7,8] Accordingly, they should compete with the *tert*-butyl group for the equatorial position when placed in the cis 4 orientation. To look for this effect in the $^{13}C$ spectra, attention should first be given to the case of the *cis*-1,4-di-*tert*-butylcyclohexane system. In a chair conformation axial character for one of the *tert*-butyls is a requirement; alternatively, ring distortion may be so great as to induce adoption of the twist conformation[22,23] as in **27**. The $^{13}C$ data for this compound[24] show no significant change for the quaternary or methyl carbons of the butyl group relative to the trans isomer, but do show upfield shifts at *C*-butyl (5.6 ppm) and the methylene carbons (4.3 ppm) in the cis isomer. These shifts clearly reveal the increased steric crowding in the cis isomer but do not necessarily imply that a change from the general chair shape to a twist shape has occurred, although $^1H$ NMR data are interpreted to be more indicative of such a change.[22] As an alternative to a twist conformation, a chair flattened at both ends needs also to be considered; such a structure has indeed been determined by x-ray analysis for *cis*-1-*p*-bromophenyl-4-*tert*-butylcyclohexane.[25] On comparing the cis phosphorus compounds **19** and **24** to the trans isomers (**17** and **22**), it is found that pronounced upfield shifts have occurred at all ring positions in the cis isomers, but seem to be the largest at atoms more controlled by the P function than by butyl. To illustrate, in the cis sulfide (**19**) C-1 is shifted 4.5 ppm upfield of the trans, and C-3,5 which would experience γ-gauche shielding by an axial P substituent are shifted 4.1 ppm upfield. At C-2,6, which are γ to butyl, an upfield shift occurs, but it is small (1.5 ppm). C-4 requires special consideration. In all of the cis isomers of the trivalent P functions, C-4 experiences a deshielding of 0.7–1.2 ppm. Since the δ effect of the tetravalent functions in the monosubstituted compounds (Table II) is in the same direction as for the trivalents, it might be expected that C-4 in the cis *tert*-butyl compounds with tetravalent phosphorus should also go downfield. In fact, the opposite is seen; C-4 is shifted *upfield* by 1.5–1.6 ppm. We attribute this to marked displacement of *tert*-butyl from the usual equatorial position, since it is just this sort of chemical shift change that is seen for *cis*-1,4-di-*tert*-butylcyclohexane. The net effect at C-4 is therefore larger than 1.5–1.6 ppm, and probably is as large as 2–3 ppm. Since this is, very roughly, about half of the shift seen at the comparable carbon in the di-*tert*-butyl compound, it is implied that the P functions have somewhat smaller *A* values than the *tert*-butyl group, consistent with our proposal of a minimum *A* value of 3.0 for the former. Crowding in the cis isomers of the sulfide and salt also produces a pronounced downfield shift in the *P*-methyl signals (2.4 and 2.2 ppm, respectively). The same effect was pointed out for the $-PMe_2$ group, although the magnitude is smaller (1.6 ppm).



**27**

The coupling of C-3,5 with $^{31}P$ sheds additional light on the conformational differences between the cis and trans forms of these compounds. This coupling is large in the trans forms **17** and **22** (13–15 Hz) and small (4 Hz) in the cis forms **19** and **24**. This clearly indicates that a considerable difference in the dihedral angle relating P to C-3,5 must be present.[17] This angle is 180° in the trans isomer in an ideal chair with ring dihedral angles of 60°. For the cis isomer, a regular chair conformation with axial P substituent results in a dihedral angle of 60°. If the cis isomer adopted a twist conformation, that with minimal nonbonded interaction would be represented by the counterpart of **27**. In this twist conformation, the dihedral angle relating P to C-3 is not the same as that relating P to C-5; in an ideal structure, one angle is 153° while the other is 169°.[26] Only the adoption of another, more crowded twist conformation than **27** would produce significantly smaller dihedral angles. At this time, the coupling evidence seems to point away from a twist conformation for the cis isomers and toward a chair conformation with axial P substituent, probably with alleviation of crowding by flattening of the ring at both ends as was found for 1-*p*-bromo-4-*tert*-butylcyclohexane.[25] With further general development of the knowledge of $^3J_{PC}$ dependence on angle relations among phosphine sulfides and phosphonium salts, it should, in principle, be possible to be more precise in the definition of the molecular geometry of these cis forms.

## Experimental Section

**General.** Proton decoupled $^{13}C$ spectra were obtained at 22.62 MHz on a Bruker HFX-10 system using the Fourier transform technique. Hexafluorobenzene in a 3-mm coaxial capillary insert served as a heteronuclear lock. Chemical shifts were determined from internal tetramethylsilane to ±0.1 ppm, while $^{13}C$–$^{31}P$ coupling constants are reported to ±1 Hz. Trivalent phosphorus compounds, except for the tertiary phosphines, were run as neat liquids. All other compounds were examined in $CDCl_3$ solution.

**Compounds.** The synthesis, properties, and $^{31}P$ chemical shifts of all compounds of this study have been reported elsewhere.[5] The $^{13}C$ NMR spectra for the series of *trans*-4-*tert*-butyl derivatives were obtained on isomer mixtures enriched to about 80–95% in this form. For phosphonous dichlorides **10** and **11**, this was accomplished by fractional distillation to give 80% trans (**10**) form. This mixture then gave similarly trans-enriched phosphines (**2** and **3**) on reduction and phosphonites (**13** and **14**) on methanolysis. Tertiary phosphines **6** and **8** were formed on reaction of the 4-*tert*-butylcyclohexyl Grignard reagent with $Me_2PCl$, with **6** constituting about 85–90% of the mixture. This ratio was maintained on sulfurization to form **17** and **19**, and methylation to **22** and **24**. Fractional distillation of the phosphonous dichlorides also provided a sample enriched to about 80% in the cis isomer (**11**) and this was used to form the entire series of cis compounds by conventional reactions.[5] For the 4-methylcyclohexyl series, a trans-rich (80–90%) tertiary phosphine mixture (**5** and **7**) resulted from the Grignard reaction, and this led to sulfide (**16** and **18**) and salt (**21** and **23**) mixtures similarly enriched. Data for the *cis*-4-methylcyclohexyl series were obtained on mixtures of nearly 1:1 cis–trans composition.

**Registry No.**—**1**, 822-68-4; **2**, 58359-91-4; **3**, 58359-90-3; **4**, 58359-87-8; **5**, 58403-25-1; **6**, 58359-93-6; **7**, 55615-34-4; **8**, 58359-92-5; **9**, 2844-89-5; **10**, 58359-95-8; **11**, 58359-94-7; **12**, 16195-98-5; **13**, 58359-97-0; **14**, 58359-96-9; **15**, 58359-88-9; **16**, 58360-05-7; **17**, 58359-99-2; **18**, 58360-04-6; **19**, 58359-98-1; **20**, 58359-89-0; **21**, 58360-07-9; **22**, 58448-99-0; **23**, 58360-06-8; **24**, 58449-00-6.

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# Organometallic Chemistry. 9.[1] Carbon-13 Nuclear Magnetic Resonance Study of the Cumylchromium Tricarbonyl and of Cycloheptatrienylmolybdenum (-chromium, and -tungsten) Tricarbonyl Cations

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The cumylchromium tricarbonyl cation was prepared under long-lived ion conditions, and studied by NMR ($^1H$ and $^{13}C$) spectroscopy. For comparison, the carbon-13 NMR parameters of three cycloheptatrienyl-$M(CO)_3$ cations (M = Mo, Cr, and W) were also determined and are reported. Based on the $^{13}C$ NMR studies the origin of the unusual stabilization of the cumylchromium tricarbonyl ion is discussed. The $\sigma^+$ substituent constant for the $Cr(CO)_3$ group and the fraction of the unit positive charge transmitted into the $M(CO)_3$ groups were qualitatively estimated.

The substituent effect of the metal tricarbonyl moiety in metal–arene complexes is of substantial interest. There is considerable evidence to show that $\pi$-complexed $Cr(CO)_3$ group exerts a net electron-withdrawing effect from the aromatic ring.[3] The deprivation of $\pi$-electron density on the aromatic ligand upon complexation with the $Cr(CO)_3$ group also appears to attenuate the substituent effect of other aryl substituents. On the other hand, the electron-releasing effect of the $Cr(CO)_3$ group has been demonstrated by the rate enhancement of solvolysis of tricarbonylchromium complexes of benzyl,[4,5] cumyl,[5] and 2-benzonorbornenyl[6] derivatives, and the increase of the $pK_{R^+}$ value for the benzylchromium tricarbonyl cation.[7] They were explained by the increase of stability of the intermediate cation with the attachment of the $Cr(CO)_3$ moiety. Previous attempts at the isolation of benzyl-, diphenylmethyl-, and triphenylmethylchromium tricarbonyl cations from the corresponding alcohols failed.[4] Upon treatment with $HClO_4$ or $HBF_4$ in $Ac_2O$, the alcohols gave only rapid decomposition. We would like to report now the preparation of the cumylchromium tricarbonyl cation **1**, the first chromium tricarbonyl complexed arylalkyl cation observed under long-lived conditions, and its $^1H$ and $^{13}C$ NMR spectroscopic study. The results provide evidence for the unusual stabilization of **1** through charge delocalization into the $Cr(CO)_3$ group. For comparison, we also determined the $^{13}C$ NMR spectroscopic parameters of three known cycloheptatrienylium–$M(CO)_3$ cations **2** (M = Mo, Cr, and W). Cations **2** represent a cyclic six $\pi$ electron aromatic system attached to a metal tricarbonyl group, whereas **1** represents a similar six $\pi$ electron system substituted by an electron-deficient exocyclic carbenium ion grouping.

## Results and Discussion

A dark-green solution of the cumylchromium tricarbonyl cation **1** was obtained upon treatment of a solution of the chromium tricarbonyl complex of cumyl alcohol with fluorosulfuric acid in $SO_2$ at −80 °C under dry nitrogen. The carbon-13 spectrum of **1** is shown in Figure 1 and the $^1H$ and $^{13}C$ NMR parameters are summarized in Tables I and II, respectively, together with the data of the corresponding ions