methyl hydrogens; the plane is tilted more toward the metal in the tg_l conformer.

Conclusion

Currently there is insufficient experimental or theoretical data available to definitely state which definition, I–IV, or which option, A–C, best represents phosphorus-ligand size. There are reasons to expect some definitions and options to be better, however.

Of options A–C, C appears to be the most fitting. When steric effects are important in complexes, a given ligand is unlikely to assume a geometry similar to the largest possible. Therefore, A is a particularly poor option, and B is the more reasonable single conformer choice. Since restricted P–C or C–C bond rotation in phosphine ligands of transition-metal complexes at room temperature is rare, a given ligand would be best described by a weighted average of the contributing conformations. Unfortunately, that information is also not experimentally available. Heat of formation data obtained from MINDO/3 has been presented here, but the reliability of the difference in conformer energies is unknown. Furthermore, the values were obtained for free ligands; relative conformer energies probably change upon complexation.

Of definitions I–IV, it is reasonable to expect that one of the averaging techniques, II–IV, is most appropriate. Definition I emphasizes the largest group and essentially ignores the smaller ones, yet there is no reason to expect, for example, that PH_2Me, $PHMe_2$, and PMe_3 are essentially the same size. Furthermore, the paucity of examples of restricted rotations about M–P bonds in trisubstituted phosphines at room temperature makes an averaging technique more reasonable. This undoubtedly contributed to Tolman's choice of definition II. It is unclear as to how much averaging is appropriate. Definition III would appear preferable to II since averaging the two gauche Me groups of g_lg_r PH_2-*i*-Pr, for example, provides a distinctly different cone angle than the average of gauche Me and H of g_r PH_2Et. Another advantage to averaging gauche groups can be visualized with PMe_3. A 5° rotation of each methyl group around the P–C bonds produces a difference of about 5° in θ_{II} but has an insignificant effect on θ_{III} or θ_{IV}. Therefore, the source of data, whether from models, X-ray crystallography, computation, or other sources, can provide inappropriate information about sizes under definition II. Definition IV has the decided advantage of not requiring the identification of gauche or substituent groups (see Idealized Conditions) but also has two important disadvantages. The extreme averaging of IV causes cone angle differences among ligands to be depressed. More important, however, is the lack of an unambiguous choice for the effective radius of phosphorus (see MINDO/3 Results subsection). If it were not for the latter problem, we would prefer definition IV, but, until the effect of phosphorus size on cone angles is clarified or sufficient data become available to make a choice obvious, we currently prefer definition III with option C.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Ball State University Faculty and Student Research grant programs for support of this research. Lois M. Ounapu, Wayne M. Zage, J. Michael McGrew, and the personnel of the Office of Research Computing are thanked for their assistance.

Registry No. PH_3, 7803-51-2; PH_2Me, 593-54-4; PH_2Et, 593-68-0; PH_2-*i*-Pr, 4538-29-8; PH_2-*t*-Bu, 2501-94-2; PH_2Ph, 638-21-1; PH_2-*o*-tol, 53772-59-1; $PHMe_2$, 676-59-5; $PHEt_2$, 627-49-6; PH(*i*-Pr)$_2$, 20491-53-6; PHMePh, 6372-48-1; PHEtPh, 3619-88-3; PMe_3, 594-09-2; PEt_3, 554-70-1; PMe_2Ph, 672-66-2.

Contribution from the Departments of Chemistry, University of Houston, Houston, Texas 77004,
and Cornell University, Ithaca, New York 14853

Conformational Effects of Nucleophilic and Electrophilic Attack on (Arene)chromium Tricarbonyl Complexes

THOMAS A. ALBRIGHT*[1a] and BARRY K. CARPENTER[1b]

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Nucleophilic and electrophilic substitution in (arene)chromium tricarbonyl complexes was investigated by means of extended Hückel molecular orbital calculations and qualitative considerations from perturbation theory. It was found that the regioselectivity of attack on the arene should be controlled not only by the substituent on the arene but also by the conformation of the $Cr(CO)_3$ unit. It is shown that the arene carbons which are eclipsed with respect to the carbonyl groups are preferentially attacked by nucleophiles. Electrophilic substitution is preferred at the staggered arene carbons. This is a consequence of the intermixing between π^* levels induced by the $Cr(CO)_3$ orbitals. Both charge and overlap controlled arguments operate in the same direction for the early stages of the reactions.

Attack by nucleophiles on (polyene)ML_n transition-metal complexes has been extensively investigated by experimental means.[2] The theoretical details of these reactions are also beginning to unfold.[3] In general, the products of nucleophilic attack are thought to be kinetically controlled with exo attack by the nucleophile on the polyene.[3c] However, there do appear to be several exceptions to this rule.[4] Of special concern to

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(1) (a) University of Houston; Camille and Henry Dreyfus Teacher-Scholar, 1979–1984. (b) Cornell University.

(2) (a) For reviews see ref 3a. Also, see: White, D. A. *Organomet. Chem. Rev., Sect. A* **1968**, *3*, 497. (b) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1975**, *102*, C4. John, G. R.; Kane-Maguire, L. A. P. *Ibid.* **1976**, *120*, C45. Mansfield, C. A.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1976**, 2187. John, G. R.; Kane-Maguire, L. A. P.; Sweigart, D. A. *J. Organomet. Chem.* **1976**, *120*, C47. Sweigart, D. A.; Wilker, C. N. *J. Chem. Soc., Chem. Commun.* **1977**, 304.

(3) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (b) Davis, S. G.; Green, M. L. H.; Mingos, D. M. P. *Nouv. J. Chim.* **1977**, *1*, 445. (c) Davis, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahdron* **1978**, *34*, 3047. (d) Ephritikhine, M.; Francis, B. R.; Green, M. L. H.; Mackenzie, R. E.; Smith, M. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1131. (e) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1976**, *107*, C40. (f) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *Ibid.* **1976**, *120*, C25. (g) Clack, D. W.; Kane-Maguire, L. A. P. *Ibid.* **1979**, *174*, 199.

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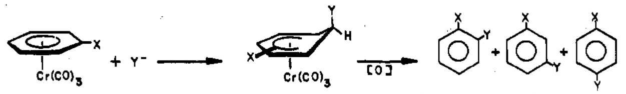
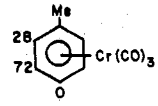


us is nucleophilic substitution on (arene)ML_n complexes[5] and (arene)$Cr(CO)_3$ complexes,[6] in particular. The addition of nucleophiles to substituted (arene)$Cr(CO)_3$ complexes, **1**, yields the exo-substituted[6h] (cyclohexadienyl)$Cr(CO)_3$ anions, **2**. Oxidation of **2** gives the corresponding free arenes. The regioselectivity of attack on **1** can be rationalized in most cases by charge density arguments.[6g] For example, when X is an electron-donating group (e.g., OMe, NMe_2), nucleophilic substitution by Y^- occurs predominantly in the meta position, giving **3b** upon oxidation. When X is an electron-withdrawing group (e.g., CF_3), attack occurs in the para position. It has also been shown[6g] that the site of attack by Y^- correlates in a qualitative sense to the magnitude of the coefficients in the LUMO of the uncomplexed arene. Regioselectivity in electrophilic and nucleophilic attack on the arenes themselves has been explained in this manner.[7] A class of compounds where these ideas fail, however, is in alkyl-substituted (arene)Cr$(CO)_3$ complexes. As the alkyl substituent becomes more bulky, para attack becomes more predominate than the expected meta one. This is shown for **4–8** where the numbers refer to the percentage of the products, **3**, formed after oxidation.[6g,j]



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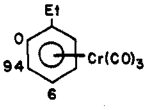

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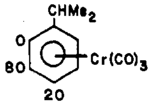

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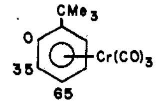

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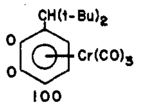
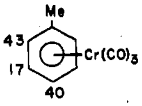


8

One could advance a steric rationalization for this trend with the provision that the alkyl groups do not substantially perturb the electronic environment of the arene; however, the dilemma runs deeper than this. Jackson and Jennings discovered an analogous trend in the acetylation of alkyl-substituted (arene)$Cr(CO)_3$ complexes.[8] As the steric bulk of the alkyl group increases, the electrophile preferentially attacks the meta position, shown in **9–12**.



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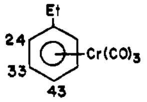

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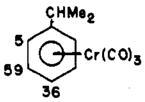

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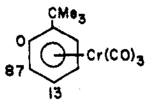

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This is again opposite to what charge density and overlap arguments in the arenes would show. *tert*-Butylbenzene as well as the other alkylbenzenes undergo acetylation almost exclusively in the para position.[8] It is not clear that electrophilic substitution of (arene)$Cr(CO)_3$ complexes occurs from the exo direction. The type of electrophilic substitution[9] most frequently studied in (polyene)ML_n[10] and (arene)ML_n[11] complexes has been

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[4] (a) Byran, E. G.; Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Schiavon, G. M. *J. Organomet. Chem.* **1977**, *129*, C19. (b) Al-Kathumi, K. M.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 1683. (c) Brown, D. A.; Chawla, S. K.; Glass, W. K. *Inorg. Chim. Acta* **1976**, *19*, L31. (d) See also for related examples: Angelici, R. J.; Blacik, L. J. *Inorg. Chem.* **1972**, *11*, 1754. Angelici, R. J.; Brink, R. W. *Ibid.* **1973**, *12*, 1067. Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919. Dobson, G. R.; Paxson, J. R. *Ibid.* **1973**, *95*, 5925. Slack, D. A.; Baird, M. C. *Ibid.* **1976**, *98*, 5539.

[5] (a) McGreer, J. F.; Watts, W. E. *J. Organomet. Chem.* **1976**, *110*, 103. Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2257, 2261; **1969**, *116*, 2024. Knipe, A. C.; McGuinness, S. J.; Watts, W. E. *J. Chem. Soc., Chem. Commun.* **1979**, 842. (b) Walker, P. J. C.; Mawby, R. J. *Inorg. Chem.* **1971**, *10*, 404. Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621. Walker, P. J. C.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 622. Walker, P. J. C.; Mawby, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 330. (c) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677, 1683. (d) Connelly, N. G.; Kelly, R. L. *Ibid.* **1974**, 2334. Ball, D. E.; Connelly, N. G. *J. Organomet. Chem.* **1973**, *55*, C24. (e) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. Winkhaus, G.; Pratt, L.; Wilkinson, G. *Ibid.* **1971**, 3807. Jones, D.; Wilkinson, G. *Ibid.* **1964**, 2479. (f) Winkhaus, G. *Z. Anorg. Chem.* **1963**, *319*, 404. Winkhaus, G.; Singer, H. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1963**, *18B*, 418. (g) Sweigart, D. A.; Kane-Maguire, L. A. P. *J. Chem. Soc., Chem. Commun.* **1976**, 13. (h) Fischer, E. O.; Schmidt, M. W. *Chem. Ber.* **1966**, *99*, 2206. (i) Efraty, A.; Maitlis, P. M. *Tetrahedron Lett.* **1966**, 4025. (j) Bird, P. H.; Churchill, M. R. *Chem. Commun.* **1967**, 777. Churchill, M. R.; Scholer, F. R. *Inorg. Chem.* **1969**, *8*, 1950. (k) Calderazzo, F. *Ibid.* **1966**, *5*, 429.

[6] (a) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 66. (b) Semmelhack, M. F.; Hall, H. T., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 7092. (c) Semmelhack, M. F.; Hall, H. T., Jr.; Yoshifuji, M.; Clark, G. *Ibid.* **1975**, *97*, 1247. (d) Semmelhack, M. F.; Hall, H. T., Jr.; Yoshifuji, M. *Ibid.* **1976**, *98*, 6347. (e) Semmelhack, M. F.; Clark, G. *Ibid.* **1977**, *99*, 1675. (f) Semmelhack, M. F.; Yoshifuji, M. *Ibid.* **1976**, *98*, 6387. (g) Semmelhack, M. F.; Clark G.; Farina, R.; Saeman, M. *Ibid.* **1979**, *101*, 217. (h) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Barger, T.; Hirotsu, K.; Clardy, J. *Ibid.* **1979**, *101*, 3535. (i) Semmelhack, M. F.; Harrison, J. J.; Thebtaranonth, Y. *J. Org. Chem.* **1979**, *44*, 3275. (j) Semmelhack, M. F., private communications.

[7] For theoretical arguments relating to overlap-controlled electrophilic and nucleophilic substitution in uncomplexed arenes see: (a) Fukui, K.; Yonezawa, T.; Shingu, H. *J. Chem. Phys.* **1952**, *20*, 722. Fukui, K.; Yonezawa, T.; Nagata, C. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 423. (b) Pedersen, E. B.; Petersen, T. E.; Torssell, K.; Lawesson, S.-O. *Tetrahedron* **1973**, *29*, 579. (c) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 3188. Epiotis, N. D.; Cherry, W. *Ibid.* **1976**, *98*, 5432. (d) Whangbo, M.-H.; Miles, M. L., to be submitted for publication.

[8] Jackson, W. R.; Jennings, W. B. *Chem. Commun.* **1966**, 824.

[9] For reviews see: Kotz, J. C.; Pedrotty, D. G. *Organomet. Chem. Rev., Sect. A* **1969**, *4*, 479. Schriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.

[10] (a) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. Brookhart, M.; Harris, D. L. *Ibid.* **1974**, *13*, 1540, 1541. (b) Falkowski, D. R.; Hunt, D. F.; Lillya, C. P.; Rausch, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 6387. (c) Birch, A. J.; Haas, M. A. *J. Chem. Soc. C* **1970**, 2465. (d) Nesmeyanov, A. N.; Ustynyuk, A.; Kritskaya, I. I.; Schembelov, G. A. *J. Organomet. Chem.* **1968**, *14*, 395. (e) Salzer, A.; Werner, H. *Ibid.* **1975**, *87*, 101. Turner, G. K.; Kläui, W.; Scotti, M.; Werner, H. *Ibid.* **1975**, *102*, C9. Werner, H.; Hofmann, W. *Angew. Chem.* **1977**, *89*, 835. (f) Hofmann, W.; Buckner, W.; Werner, H. *Angew. Chem.* **1977**, *89*, 836. (g) Ginzburg, A. G.; Okulevich, P. O.; Setkina, V. N.; Panosyan, G. A.; Kursanov, D. N. *J. Organomet. Chem.* **1974**, *81*, 201. Ginzburg, A. G.; Fedorov, L. A.; Petrovskii, P. V.; Fedin, E. I.; Setkina, V. N.; Kursanov, D. N. *Ibid.* **1974**, *73*, 77. Pyshnograyeva, N. I.; Setkina, V. N.; Panosyan, G. A.; Petrovskii, P. V.; Makarov, Yu. V.; Kolobova, N. E.; Kursanov, D. N. *Ibid.* **1976**, *108*, 85. Panosyan, G. A.; Petrovskii, P. V.; Pyshnograyeva, N. I.; Kolobova, N. E.; Setkina, V. N.; Fedin, E. I. *Ibid.* **1976**, *108*, 209. Lokshin, B. V.; Pasinsky, A. A.; Kolobova, N. E.; Anisimov, K. N.; Markarov, Yu. V. *Ibid.* **1973**, *55*, 315. Ginzburg, A. G.; Setkina, V. N.; Kursanov, D. N. *Ibid.* **1979**, *182*, C1. (h) Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *J. Chem. Soc., Dalton Trans.* **1972**, 2084. Evans, J.; Johnson, B. F. G.; Lewis, J. *Ibid.* **1972**, 2668. Johnson, B. F. G.; Lewis, J.; Yarrow, D. J. *Ibid.* **1974**, 1054. (i) Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296. (j) Cowherd, F. G.; von Rosenberg, J. L. *Ibid.* **1969**, *91*, 2157. (k) Gibson, D. H.; Vannahme, R. L. *Ibid.* **1972**, *94*, 5090; *J. Chem. Soc., Chem. Commun.* **1972**, 1021. (l) Young, D. A. T.; Holmes, J. R.; Kaesz, H. D. *J. Am. Chem. Soc.* **1969**, *91*, 6968. (m) Olah, G. A.; Yu, S. H.; Liang, G. *J. Org. Chem.* **1976**, *41*, 2383. Olah, G. A.; Liang, G.; Yu, S. H. *Ibid.* **1976**, *41*, 2227. Olah, G. A.; Liang, G. *Ibid.* **1976**, *41*, 2660. Olah, G. A.; Liang, G.; Yu, S. H. *Ibid.* **1977**, *42*, 4262. (n) Cerichelli, G.; Illuminati, G.; Ortaggi, G.; Giuliani, A. M. *J. Organomet. Chem.* **1977**, *127*, 357. (o) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4814. (p) Flood, T. C.; Rosenberg, E.; Sarhangi, A. *Ibid.* **1977**, *99*, 4334. (q) Ittel, S. D.; Van-Catledge, F. A.; Jesson, J. P. *Ibid.* **1979**, *101*, 6905.

protonation. In nearly all cases it has been demonstrated that the proton initially attacks the metal. Acetylation of (butadiene)Fe(CO)$_3$ also probably first occurs by attack of the electrophile on the metal.[12] However, not much is experimentally known about the mechanism of electrophilic substitution on (arene)Cr(CO)$_3$ compounds with bulky electrophiles. We have found that the regiochemistry in these cases can be explained if one assumes direct attack of the electrophile on the arene ring, vide infra. Whether this occurs from the endo or exo direction with respect to the metal will make no difference in our analysis.

The presence of the Cr(CO)$_3$ unit must dictate why nucleophilic substitution proceeds para and electrophilic substitution meta in (*tert*-butylbenzene)Cr(CO)$_3$. We shall show how this comes about with the aid of molecular orbital calculations of the extended Hückel type, as well as the importance of the conformation of the Cr(CO)$_3$ unit in directing nucleophilic attack for other substituted arene complexes. To do this we need to derive the important valence orbitals of (benzene)Cr(CO)$_3$. This is done in Figure 1 by the interaction of the π orbitals of benzene with those of Cr(CO)$_3$.

The valence orbitals of the Cr(CO)$_3$ fragment shown on the right side of Figure 1 have been given in detail elsewhere.[13,14] 1e and 1a$_1$ are readily identifiable with the t$_{2g}$ and 2e with e$_g$ in Cr(CO)$_6$. 2a$_1$ is a hybrid orbital chiefly of s, z, and z^2 character.[15] Another way to view 2e and 2a$_1$ is to regard them as the three symmetry-adapted hybrid orbitals derived from the removal of three *fac* carbonyls, from Cr(CO)$_6$. The 1e set is primarily δ in character, $x^2 - y^2$ and xy, using the coordinate system in Figure 1. There is also some π character, xz and yz, mixed in. Likewise, 2e is chiefly of π character with some δ mixed in. The intermixing of δ and π "tilts" the 1e and 2e set. It is this tilting of M(CO)$_3$ which gives rise to rotational barriers in (polyene)M(CO)$_3$ complexes.[14] Now the lowest π orbital of benzene, 1a$_1$, interacts with 1a$_1$ and 2a$_1$ of Cr(CO)$_3$ to produce a set of three orbitals. The two orbitals at lowest energy which are shown in Figure 1 are filled. The 1e set on Cr(CO)$_3$ is stabilized by benzene 2e, π^*, and destabilized by a high-lying σ set which is also of δ symmetry. The benzene π, 1e, set is stabilized greatly by 2e of Cr(CO)$_3$.

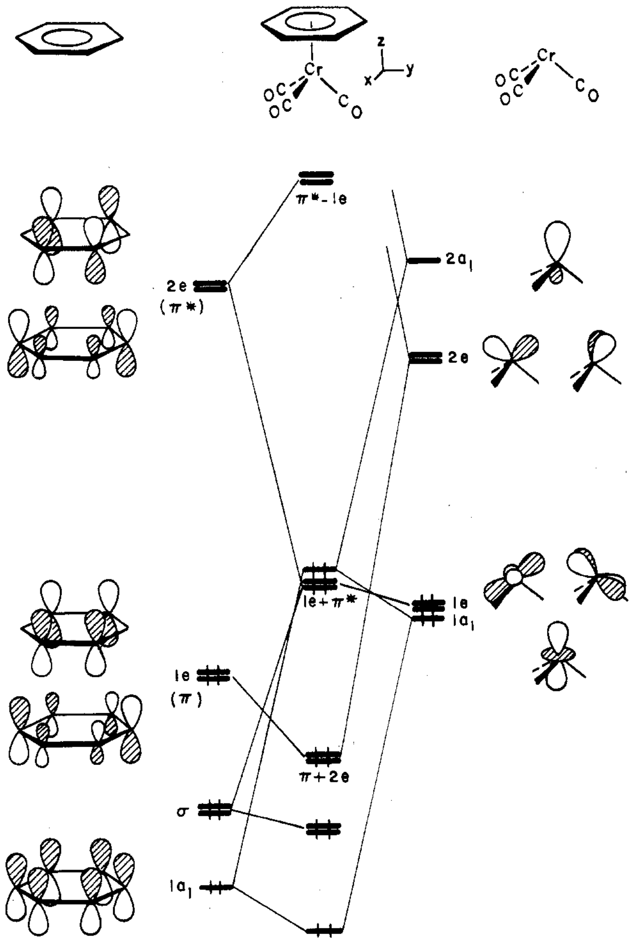

Figure 1. Interaction diagram for (benzene)Cr(CO)$_3$.

These two molecular levels, 1e + π^* and π + 2e, will figure into our discussion of nucleophilic attack along the lowest occupied molecular orbital (LUMO), the antibonding combination of π^* with 1e, π^* − 1e. The antibonding interaction of π with 2e, 2e − π, not shown on Figure 1 lies at much higher energy. In an extended Hückel calculation, with details given in the Appendix, 2e − π lies approximately 3 eV higher in energy than the LUMO, π^* − 1e. This is a result of the much larger π overlap of 2e with π than the δ overlap between 1e and π^* (the group overlaps[16] are 0.270 and 0.111, respectively). A further consequence of the larger π overlap is that more electron density is transferred from the π level to 2e in Cr(CO)$_3$ than that from Cr(CO)$_3$ 1e to benzene π^*. From our calculations a net 0.397 electron is transferred from benzene to Cr(CO)$_3$. While this number is not expected to be quantitatively reliable, it highlights the remarkable electron deficiency of complexed arenes and their susceptibility to nucleophilic attack. The three high-lying, filled molecular orbitals of (benzene)Cr(CO)$_3$ in Figure 1 are mainly concentrated on the metal. Thus a small electrophile like the proton is expected to directly attack the metal.

The preceding discussion was done without regard to the conformation in (benzene)Cr(CO)$_3$. There are two, the staggered and eclipsed, conformations shown from a top view along the z axis in **13** and **14**, respectively. In (arene)Cr(CO)$_3$ complexes there are two additional conformations, the anti-eclipsed and syn-eclipsed conformations, **15** and **16**, respectively. There is only a tiny energy difference[14a] between the

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(11) (a) Lillya, C. P.; Sahatjian, R. A. *Inorg. Chem.* **1972**, *11*, 889. (b) Anderson, W. P.; Hsu, N.; Stanger, C. W., Jr.; Munson, B. *J. Organomet. Chem.* **1974**, *69*, 249. (c) Olah, G. A.; Yu, S. H. *J. Org. Chem.* **1976**, *41*, 717. (d) Kursanov, D. N.; Setkina, V. N.; Petrovskii, P. V.; Zdanovich, V. I.; Baranetskaya, N. K.; Rubin, I. D. *J. Organomet. Chem.* **1972**, *37*, 339. Lokshin, B. V.; Ginzburg, A. G.; Setkina, V. N.; Kursanov, D. N.; Nemirovskaya, I. B. *Ibid.* **1972**, *37*, 347. Lokshin, B. V.; Zdanovich, V. I.; Baranetskaya, N. K.; Setkina, V. N.; Kursanov, D. N. *Ibid.* **1972**, *37*, 331. Fedorov, L. A.; Petrovskii, P. V.; Fedin, E. I.; Baranetskaya, N. K.; Zdanovich, V. I.; Setkina, V. N.; Kursanov, D. N. *Ibid.* **1975**, *99*, 297. Setkina, V. N.; Baranetskaya, N. K.; Ginzburg, A. G.; Zdanovich, V. I.; Nefedova, M. N.; Kursanov, D. N. *Ibid.* **1973**, *61*, 287. Baranetskaya, N. K.; Zdanovich, V. I.; Mysov, E. I.; Kolobova, N. E.; Anisimov, K. N.; Setkina, V. N.; Kursanov, D. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 758. Zdanovich, V. I.; Yakushin, F. S.; Setkina, V. N.; Baranetskaya, N. K.; Kursanov, D. N.; Shatensktein, A. I. *Ibid.* **1974**, 1655. (e) Green, M. L. H.; Mitchard, L. C.; Silverton, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1361.

(12) (a) Graf, R. E.; Lillya, C. P. *J. Am. Chem. Soc.* **1972**, *94*, 8282. (b) Hardy, A. D. U.; Sim, G. A. *J. Chem. Soc., Dalton Trans.* **1972**, 2305. (c) Greaves, E. O.; Knox, G. R.; Pauson, P. L. *Chem. Commun.* **1969**, 1124. Greaves, E. O.; Knox, G. R.; Pauson, P. L.; Joma, S.; Sim, G. A.; Woodhouse, D. I. *J. Chem. Soc., Chem. Commun.* **1974**, 257. (d) Johnson, B. F. G.; Lewis, J.; Quail, J. W. *J. Chem. Soc., Dalton Trans.* **1975**, 1252.

(13) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Ibid.* **1976**, *15*, 1148. Burdett, J. K. *Ibid.* **1975**, *14*, 375; *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599.

(14) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1578. (c) Albright, T. A.; Hofmann, P.; Hoffmann, R. *Ibid.* **1978**, *111*, 1591. (d) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1.

(15) We use the notation $x^2 - y^2$, z^2, xy, xz, yz for the nd orbitals and x, y, z for the $(n + 1)$p orbitals.

(16) The methodology used for this fragment molecular orbital analysis is given by: Hoffmann, R.; Fujimoto, H.; Swenson, J. R.; Wan, C.-C. *J. Am. Chem. Soc.* **1973**, *95*, 7644. Fujimoto, H.; Hoffmann, R. *J. Phys. Chem.* **1974**, *78*, 1167.

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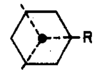
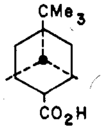


16

staggered and eclipsed conformations in (benzene)$Cr(CO)_3$. This has been experimentally established to be the case from electron diffraction data.[17] Our calculations give the staggered form to be 0.3 kcal/mol more stable. **13** is found to be the conformation in the X-ray and neutron diffraction studies[18] of (benzene)$Cr(CO)_3$. There are also two structures of isoelectronic η^6-$C_6H_6RuL_3$ which are eclipsed and one structure which is staggered.[19] This again implies a very low rotational barrier. Substituted (benzene)$Cr(CO)_3$ complexes fall neatly into two classes. When R is an electron-donating group the syn-eclipsed structure, **16**, is normally found.[20] The anti-eclipsed conformation, **15**, is observed when R is an electron-withdrawing group.[20e,21] A detailed discussion of the electronic factors behind these conformational preferences has been given elsewhere.[14a] The rotational barriers in (arene)-$Cr(CO)_3$ complexes are, however, still quite small. For example syn-eclipsed (aniline)$Cr(CO)_3$ is calculated to be 1.3 kcal/mol more stable than the anti-eclipsed structure.[14a] Other evidence for small barriers comes from the fact that intermolecular packing effects sometimes dictate the conformation. There are four examples of (methyl benzoate)CrL_3 complexes which adopt the expected anti-eclipsed conformation[21a–c,e] and one structure[22] which has the staggered conformation. (Acetophenone)$Cr(CO)_3$ also adopts the staggered conformation.[23] Intramolecular steric factors must likewise play a role. The predicted structure of (*p-tert*-butylbenzoic acid)$Cr(CO)_3$ is **17**. However, a nearly staggered structure



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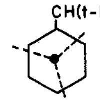


18

is found.[24] More significantly, the structure of **18** is rotated 44° away from its expected syn-eclipsed form.[25] There exist three structures[20c,d] of bis(*o*-alkylbenzene)$Cr(CO)_3$ complexes, and in each case the chromium carbonyl group was found to eclipse the sterically least bulky alkyl group. Dipole moments,[26] pK_a,[27] and especially NMR effects[28] have been studied with regard to the orientation of the $Cr(CO)_3$ group.

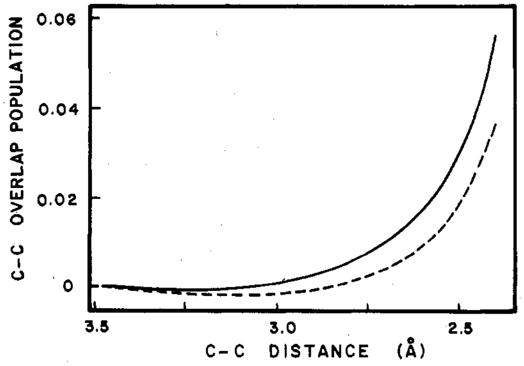
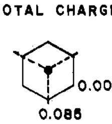


Figure 2. Change in carbon–carbon overlap population as a function of internuclear distance for a methyl carbanion attacking eclipsed (benzene)$Cr(CO)_3$. The solid line refers to path 1 and the dashed to path 2 as defined by **22** in the text.

In the staggered conformation of (benzene)$Cr(CO)_3$ all carbons on the arene are equivalent. However, in the eclipsed geometry, **14**, three carbons are eclipsed by chromium–carbonyl bonds and three are staggered; therefore, the arene carbons now form two nonequivalent sets. An extended Hückel calculation on eclipsed (benzene)$Cr(CO)_3$ gives the charges on these carbons as shown in **19**. If nucleophilic and electrophilic substitution are charge-controlled reactions, then this result implies that in the absence of any electronic effects from the arene nucleophiles will attack arene carbons which eclipse chromium–carbonyl bonds and electrophiles will attack staggered arene carbons. The densities in the LUMO, $\pi^* - 1e$ combination, are given in **20**. The coefficients of the atomic orbitals in the arene carbons are polarized so that they are larger at the eclipsed carbons. If nucleophilic attack is overlap controlled, then our calculations point to a definite preference for attack at the eclipsed arene carbons. The densities in the $1e + \pi^*$ and $\pi + 2e$ levels are polarized in the opposite direction. The total of both is shown in **21**. Thus, overlap considerations would lead to the prediction of electrophilic substitution at the staggered carbons. If only the atomic *z* contributions (see Figure 1 for the coordinate system) are considered, then the polarization evident in **19**–**21** becomes even greater.



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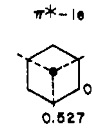

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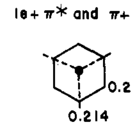

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A model calculation of a methyl carbanion attacking eclipsed (benzene)$Cr(CO)_3$ during the early stages of the reaction also shows the results outlined above. In the two

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[17] Chiu, N.-S.; Schäfer, L.; Seip, R. *J. Organomet. Chem.* **1975**, 101, 331.

[18] (a) Bailey, M. F.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1314, 1298. (b) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2516.

[19] Chan, L. Y. Y.; Graham, W. A. G. *Inorg. Chem.* **1975**, *14*, 1778. Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J.; Lalor, F. J. *Ibid.* **1975**, *14*, 3046. Bennett, M. A.; Robertson, G. B. *J. Organomet. Chem.* **1972**, *43*, C41.

[20] (a) Carter, O. L.; McPhail, A. T.; Sim, G. A. *Chem. Commun.* **1967**, 288; *J. Chem. Soc. A* **1966**, 822. (b) Dusausoy, Y.; Protas, J.; Besaneon, J.; Tirouflet, J. *Acta Crystallogr., Sect. B* **1972**, *B28*, 3183. (c) Dusausoy, Y.; Protas, J.; Besancon, J. *J. Organomet. Chem.* **1973**, *59*, 281. (d) Dusausoy, Y.; Lecomte, C. *Ibid.* **1973**, *63*, 321. (e) Dusausoy, J.; Protas, J.; Besancon, J.; Tirouflet, J. *Acta Crystallogr., Sect. B* **1973**, *B29*, 469. (f) van Meurs, F.; von Koningsveld, H. *J. Organomet. Chem.* **1977**, *131*, 423. (g) Koshland, D. E.; Myers, S. E.; Chesick, J. P. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2013.

[21] (a) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1967**, 1619. (b) Andrianov, V. G.; Struchkov, Yu. T.; Baranetskaya, N. K.; Setkina, V. N.; Kursanov, D. N. *J. Organomet. Chem.* **1975**, *101*, 209. (c) Saillard, J.-Y.; LeBorgne, G.; Grandjean, D. *Ibid.* **1975**, *94*, 409. (d) Dusausoy, Y.; Protas, J.; Besancon, J.; Top, S. *Ibid.* **1975**, *94*, 47. (e) Saillard, J.-Y.; Gradjean, D. *Acta Crystallogr., Sect. B* **1976**, *32*, 2285. (f) Taylor, I. F., Jr.; Griffith, E. A. H.; Amma, E. L. *Ibid.* **1976**, *32*, 653. (g) Dotz, K. H.; Dietz, R.; von Imhof, A.; Lorenz, H.; Huttner, G. *Chem. Ber.* **1976**, *109*, 2033. (h) Bush, M. A.; Dullforce, T. A.; Sim, G. A. *Chem. Commun.* **1969**, 1491.

[22] Le Maux, P.; Simonneaux, G.; Joeuen, G.; Quahab, L.; Batail, P. *J. Am. Chem. Soc.* **1978**, *100*, 4321.

[23] Dusausoy, Y.; Protas, J.; Besancon, J.; Tirouflet, J. *C. R. Hebd. Seances Acad. Sci.* **1970**, *270*, 1792.

[24] van Meurs, F.; van Konigsveld, H. *J. Organomet. Chem.* **1974**, *78*, 229.

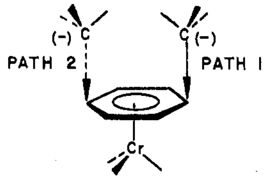
[25] van Meurs, F.; van Konigsveld, H. *J. Organomet. Chem.* **1976**, *118*, 295.

[26] Lumbrosco, H.; Segard, C.; Roques, B. *J. Organomet. Chem.* **1973**, *61*, 249.

[27] Ashraf, M.; Jackson, W. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 103.

[28] (a) Segart, C.; Roques, B. P.; Pommier, C.; Guiochon, G. *Anal. Chem.* **1971**, *43*, 1146. Roques, B. P.; Segart, C.; Combrisson, S.; Wehrli, F. *J. Organomet. Chem.* **1974**, *73*, 327. (b) van Meurs, F.; van der Toorn, J. M.; van Bekkum, H. *Ibid.* **1976**, *113*, 341. (c) Jackson, W. R.; Jennings, W. B.; Spratt, R. *Chem. Commun.* **1970**, 593. Gracey, D. E. F.; Jackson, W. R.; Jennings, W. B.; Rennison, S. C.; Spratt, R. *J. Chem. Soc. B* **1969**, 1210. Jackson, W. R.; Jennings, W. B.; Rennison, S. C.; Spratt, R. *Ibid.* **1969**, 1214. Jackson, W. R.; Pincombe, C. F.; Rae, I. D.; Thapebinkarn, S. *Aust. J. Chem.* **1975**, *28*, 1535. (d) Emanuel, R. V.; Randall, E. W. *J. Chem. Soc. A* **1969**, 3002. (e) Barbieri, G.; Taddei, F. *Chem. Commun.* **1970**, 312. (f) See also for related material: Fedorov, L. A.; Petrovskii, P. W.; Fedin, E. I.; Panosyan, G. A.; Tsoi, A. A.; Baranetsakya, N. K.; Setkina, V. N. *J. Organomet. Chem.* **1979**, *182*, 499.

possible paths of approach, labeled paths 1 and 2 in **22**, the



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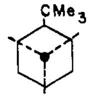
methyl carbanion was brought at an angle of 90° with respect to the benzene plane. Figure 2 plots the total carbon–carbon overlap population between the methyl carbanion and benzene carbon as a function of their internuclear separation. The solid line refers to path 1 where the carbanion attacks a benzene carbon which is eclipsed by a chromium–carbonyl bond. The dashed line represents path 2, attack on a staggered benzene carbon. Throughout the initial stages of the reaction, path 1 shows greater bonding between the carbons. While the energies between the two paths should not be considered quantitatively reliable from our calculations, path 1 is also favored throughout the early stages of the reaction. At a carbon–carbon distance of 2.4 Å, path 1 is favored by 1.6 kcal/mol. Finally, the HOMO is mainly the lone-pair orbital of the methyl group interacting with benzene π and π^*. The energy of the HOMO also favors path 1.[29]

The *tert*-butyl group is electron donating;[30] however, the steric bulk of it forces the $Cr(CO)_3$ group away from the electronically favored syn-eclipsed conformation toward the less encumbered anti-eclipsed form, **23**.[31] We feel that the



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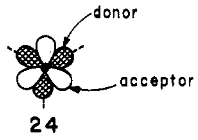
$Cr(CO)_3$ group directs nucleophilic and electrophilic substitution on the arene ring more strongly than does the *tert*-butyl group. Therefore, nucleophiles are favored to attack para and electrophiles meta in such a situation. We shall return to an examination of the strength of the $Cr(CO)_3$ group in dictating regioselectivity shortly. But first let us look at why $Cr(CO)_3$ polarizes the coefficients (and electron density) in the benzene ring the way it does.

A simple explanation of why the carbons eclipsed by chromium–carbonyl bonds are electron deficient compared to the staggered ones can be developed: 1e and $1a_1$ in Figure 1 can be hybridized into three donor orbitals.[14a] 2e and $2a_1$ are used to form three acceptor functions. A top view of these hybrids is shown in **24**.[32] Putting the $Cr(CO)_3$ group on the



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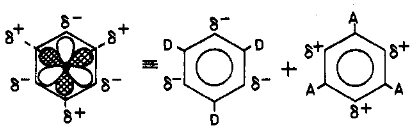
benzene in the eclipsed manner causes the charge distribution in **25**—a superposition of **26** and **27** where D is an electron

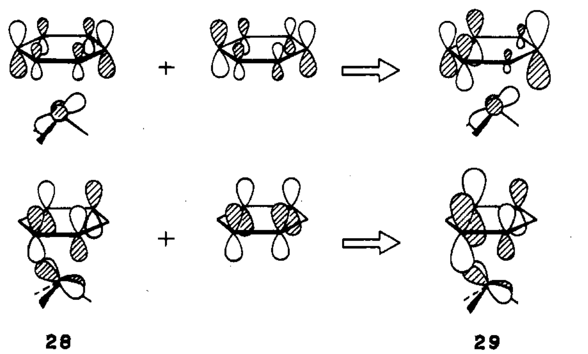


25 **26** **27**

donor and A an electron acceptor. In terms of our frontier orbital argument since charge is built up in the occupied levels on staggered carbons, then the coefficients at the eclipsed carbons will be increased in the unoccupied orbitals. A theoretically more rigorous way to construct the polarization in the relevant orbitals is by utilizing second-order perturbation theory.[33] This has been elegantly used to examine the regioselectivity of nucleophilic attack in (allylcyclopentadienyl)MLL′ by Schilling, Hoffmann, and Faller.[3a] With reference to Figure 1 all of the overlaps between the fragments are in-phase except that between 2e and π^*. Let us first consider the LUMO, $\pi^* - 1e$. The main, first-order interaction occurs between π^* and 1e as we have drawn in Figure 1. However, the overlap between 1e and π is nonvanishing—some π character is mixed into the predominantly δ 1e set. Therefore, π can mix into π^* by means of 1e. This matrix element will be of the form

$$C''_{\pi,\pi^*} \propto \frac{\langle\pi|1e\rangle\langle 1e|\pi^*\rangle}{(\epsilon^0_{\pi^*} - \epsilon^0_{\pi})(\epsilon^0_{\pi^*} - \epsilon^0_{1e})} = \frac{(+)(+)}{(+)(+)} = (+)$$

Here ϵ^0_j represents the starting fragment orbital energies and C''_{ij} the mixing of orbital i into j to second order. In the $\pi^* - 1e$ level, **28**, π will mix with the same phase as shown in Figure 1 to give **29**.[34] The coefficients at benzene become



28 **29**

larger on the eclipsed carbons, giving the polarization evident in **20**. In the 1e + π^* level, π^* mixes into 1e in a bonding manner, **30**, since π^* lies at higher energy. However, π will mix into the level in an antibonding way since it is lower in energy than 1e. The resultant orbitals are given by **31**. The second-order mixing of π^* into π by way of 2e in the π + 2e level is in the same sense as **31**—the coefficients are increased on the staggered carbons. This same methodology can be used to show why the carbon–carbon bonds eclipsing the chromium–carbonyl bonds are longer[18b] in staggered (benzene)$Cr(CO)_3$ than the staggered ones.

The careful reader will have noted that, since donor-substituted (arene)$Cr(CO)_3$ complexes prefer the syn-eclipsed rotomer, **16**, the effects of the $Cr(CO)_3$ conformation and

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(29) Calculations were also carried out at various geometries with the methyl carbanion attacking the metal. A very repulsive surface was encountered. This is primarily a consequence of 1e and $1a_1$ of the $Cr(CO)_3$ repelling the methyl lone pair. The early stages of reaction between a proton and (benzene)$Cr(CO)_3$ favor an approach toward the metal between the y and z axis (see Figure 1) in the negative direction over attack on the benzene ring.

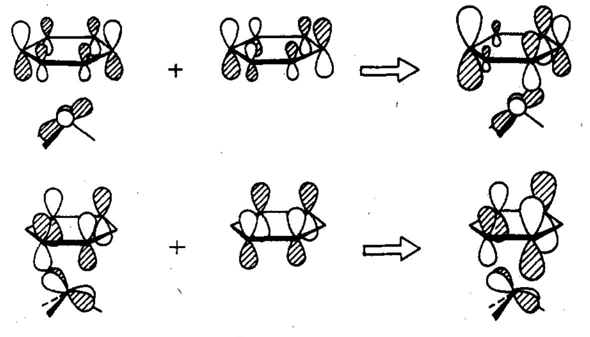
(30) Acylation in *tert*-butylbenzene occurs almost exclusively para: Brown, H. C.; Marino, C. *J. Am. Chem. Soc.* **1959**, *81*, 5611.

(31) Some NMR information has been interpreted in this light: see ref 28c.

(32) For the importance of these hybrids in dictating the conformation of L_3M–ML_3 and $L_3MH_3ML_3$ dimers, see: Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 7736. Dedieu, A.; Albright, T. A.; Hoffmann, R. *Ibid.* **1979**, *101*, 3141.

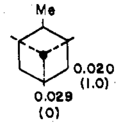
(33) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370. Imamura, A. *Mol. Phys.* **1968**, *15*, 225.

(34) There will be another matrix element representing the mixng of π into π^* by way of 2e. The sign of this element is opposite to that of the π into π^* by way of 1e mixing. Our calculations show that the latter is dominant. The reason behind this lies in a comparison of $\langle 1e|\pi\rangle$ vs. $\langle 2e|\pi^*\rangle$, 0.066 and 0.024, respectively. Any x and y character mixed into 1e or 2e has a nonvanishing overlap only with π—not π^*. There is much more x and y character built into 2e than 1e. This dilutes the δ component of 2e.



30 **31**

electronic effects of the donor group operate in concert. Nucleophilic substitution is directed meta. The same relationship holds for acceptor-substituted (arene)Cr(CO)$_3$ complexes, but just how strong is the regioselectivity imposed by the Cr(CO)$_3$ group? Experimentally and theoretically this is difficult to quantify, and, indeed, our calculations at the extended Hückel level should only be regarded in a qualitative sense. Calculations were carried out on (toluene)-, (aniline)-, and (phenylborane)Cr(CO)$_3$. The early stages of attack on the meta and para positions by the methyl carbanion were used to examine this. The methyl group was again brought in perpendicular to the arene plane. The trends were identical throughout the course of the reaction studied: carbon–carbon distances from 3.9 to 2.5 Å. The carbon–carbon overlap populations are shown in **32**–**34** for a carbon–carbon distance of 2.5 Å. The numbers in parentheses are the relative total energies in kcal/mol. Notice that in **32**–**34** the orientation of the Cr(CO)$_3$ group is in the *wrong* direction. The favored direction of attack is para in **32** and **33** and meta in **34** by both sets of criteria. In other words, the Cr(CO)$_3$ group is predicted to be a stronger electronic factor than any of the substituents. The overlap populations and relative energies of the complexes in their preferred conformations are shown in **35**–**37**. The direction of attack is now reversed. Within a given complex the most favored mode of attack occurs meta for (toluene)- and (aniline)Cr(CO)$_3$ and para for (phenylborane)Cr(CO)$_3$ with the conformations given for **35**–**37**. The energy difference between meta attack in **35** and **36** compared to para attack in **32** and **33** was 0.2 and 1.3 kcal/mol, respectively. The corresponding difference between para in **37** and meta in **34** was 2.4 kcal/mol.



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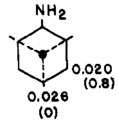

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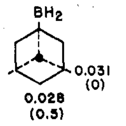

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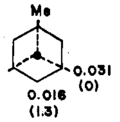

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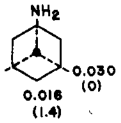

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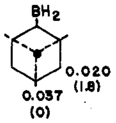

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As we have previously mentioned, in most cases the effect of a substituent couples itself with that of the Cr(CO)$_3$ group. It is, only when the steric bulk of the substituent is large (e.g., *t*-Bu or (*t*-Bu)$_2$CH), that a seemingly anomalous substitution product will be likely to occur. Factors other than conformational also may play a significant and even dominant role. For example, at the present time it is difficult to explain the increasingly stronger ortho preference as the nucleophile becomes smaller in (toluene)Cr(CO)$_3$,[6j] yet the amount of para product remains minimal. Likewise, the strong regioselectivity in (*o*-dimethoxybenzene)Cr(CO)$_3$ and (naphthalene)Cr(CO)$_3$ cannot be due to the conformational effects of the Cr(CO)$_3$ group. These three compounds are currently under additional experimental and theoretical scrutiny. Other (polyene)M(CO)$_3$ complexes also show some, albeit smaller, polarization of the π levels in a selective manner with respect to the orientation of the M(CO)$_3$ group. Examples that we have investigated include (cycloheptatrienyl)-, (cyclopentadienyl)-, and (cyclobutadiene)M(CO)$_3$. The larger polarization in the arene series comes from that fact that the three donor and three acceptor groups, **24**, on Cr(CO)$_3$ *each* point to a different arene carbon. This is not possible for the other examples. ML$_2$ and C_{4v} ML$_4$ complexes of butadiene and benzene[35] will also show a substantial charge imbalance in the carbons of the polyene. Since the orbitals of a (benzene)M or (cyclopentadienyl)M fragment are not tilted,[14a] arene complexes of them will not show this conformational effect.

Table I. Parameters Used in the Extended Hückel Calculations

orbital		H_{ii}, eV	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
Cr	3d	−11.22	4.95	1.60	0.4876	0.7205
	4s	−8.66	1.70			
	4p	−5.24	1.70			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
B	2s	−15.20	1.30			
	2p	−8.20	1.30			
N	2s	−26.00	1.95			
	2p	−13.40	1.95			
O	2s	−32.30	2.275			
	2p	−14.80	2.275			
H	1s	−13.60	1.30			

^{a} Contraction coefficients used in the double-ζ expansion.

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Appendix

All calculations were performed by using the extended Hückel method.[36] A modified Wolfsberg–Helmolz formula was used.[37] The parameters listed in Table I have been taken from earlier work.[14a] The distance of Cr to the arene ring was set at 1.73 Å. The Cr–CO and C–O distances were 1.84 and 1.13 Å, respectively. The C(O)–Cr–C(O) angles were fixed at 90° and all internuclear angles in the arene ring at 120°. The C–C and C–H distances were 1.41 and 1.09 Å, respectively. The C–CH$_3$, C–B, and C–N distances used were 1.52, 1.54, and 1.40 Å, respectively.

Registry No. **4**, 12083-24-8; **5**, 12203-31-5; **6**, 12203-34-8; **7**, 12110-51-9; **8**, 60502-70-7; **33**, 12108-11-1; **34**, 74381-38-7; (C$_6$H$_6$)Cr(CO)$_3$, 12082-08-5.

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(35) For a discussion of the electronic structures in these compounds and their distortion, see: Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *Ibid.* **1979**, *101*, 3812. Radonovich, L.; Albright, T. A., submitted for publication.

(36) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 3179, 3489; **1962**, *37*, 2872. Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.