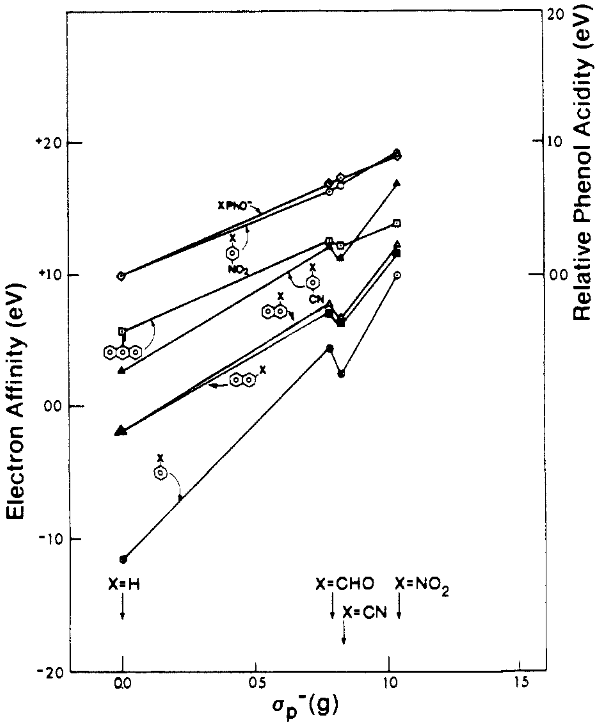
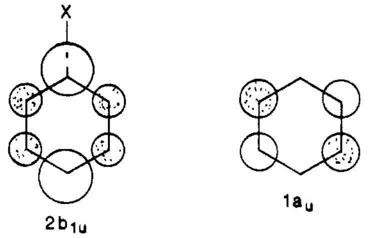


Figure 1. Electron affinities of benzenes, naphthalenes, anthracenes, cyanobenzenes, and nitrobenzenes with substituents X (H, HCO, CN, NO_2), vs. Hammet-type substituent constants σ_p^-(g) based on gas-phase acidities of phenols, PhOH; see Taft.[10] The free energy change for the proton transfer $PhO^- + X\text{-}PhOH = PhOH + X\text{-}PhO^-$ is shown on the right-side ordinate. Electron affinities for benzaldehyde and benzonitrile are from Chen and Wentworth,[9a,b] benzene and naphthalene from Jordan,[9c,d] and other values from present laboratory.

stronger than CHO, electron-withdrawing effect is observed; see Figure 1.

The Hückel type SOMO orbitals for the benzene negative ion are shown as



Radom[12] has performed STO-3G calculations for several singly substituted benzene radical anions. He points out that electron-withdrawing substituents like CHO, CN, and NO_2 will lead to preference for the $2b_{1u}$ π^* orbital as the SOMO orbital since this orbital has high electron density in the ipso position of the substituent, whereas the otherwise equivalent $1a_u$ orbital has a node and thus zero electron density at this position. This means that the $2b_{1u}$ orbital can much better provide π-type electrons to feed the π-electron-withdrawing X and also provide nearby electron charge to interact with the dipole of X (field effect). The calculations of Radom[13] predict, for the benzo anions $C_6H_5X^-$, a higher SOMO electron density on X = CHO (0.528e) relative to X = CN (0.160e). The separation of Taft and co-workers[10] of the substituent effect (Table V, ref 10) into resonance *R* and inductive *I* effects, based on phenol gas-phase acidities and calculations, assigns a large-electron-withdrawing *R* effect (−9.2) and a small-electron-withdrawing *I* (−6.6) effect to CHO group, while for CN the opposite assignment of a small *R* (−4.5) and a large *I* (−12.1) is made. We note that the larger *R* effect for CHO is parallel to the Radom-calculated larger SOMO π density for the CHO group of the benzaldehyde anion relative to CN in the benzonitrile anion.

The observation that the CHO substituent has a stronger stabilizing effect relative to CN in the radical anions with large SOMO π^* electron densities in the ring and the reversal of the effect as the density is decreased, see Figure 1, indicate that the π withdrawal (*R* effect) is much more strongly attenuated with decreasing SOMO ring density than the inductive effect. Since the *I* effect is largely an electrostatic field effect,[13] which for the radical anions corresponds to a stabilization due to the attraction between the dipole of the substituent and the SOMO electron charge outside the substituent, the electrostatic energy terms could in principle be evaluated by calculation.[14] Further experimental confirmation of the above observations is available from measured electron affinities[6] of nitrobenzenes and cyanobenzenes substituted with a larger variety of substituents. These show that substituents whose effect is mostly due to a field-inductive stabilization, e.g., CF_3, increase the electron affinity of cyano- and nitrobenzene by nearly an equal amount.

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Hybridization Effects on Metal–Ligand Bond Lengths in Organometallic Compounds

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Single bonds to sp^2-hybridized carbon centers are shorter than those to sp^3 centers, and linkages to sp carbons are shorter still. The phenomenon is general and well documented.[1] The theoretical[2] and experimental data in Table I illustrate the magnitude of the effect for bonds between carbon in its three common hybridization states and hydrogen, methyl, fluoro, silyl, and chloro substituents. Bond-length reductions are less for rehybridization from sp^3 to sp^2 carbon than from sp^2 to sp, consistent with a lesser change in p character, i.e., 25% to 33% vs. 33% to 50%.

Bond-length changes resulting from rehybridization at carbon may be attributed to differences in the radial extensions of valence s- and p-type orbitals, specifically the fact that valence p functions are more diffuse than the corresponding s-type functions. In this paper, we suggest that these same principles apply to the description of the bonding in transition-metal organometallic compounds.

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(1) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper and Row: New York, 1983; pp 113–121.

(2) All calculations have been performed at the single determinant level by using the split-valence 3-21G basis set[3] (3-21G(*) for second-row elements[3c]). The GAUSSIAN 85 program system has been used throughout.[4]

(3) First row: (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Second row: (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2779. (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkely, J. S. *Ibid.* **1982**, *104*, 5039. Third- and fourth-row main group: (d) Dobbs, K. D.; Hehre, W. J. *J. Comput. Chem.*, in press. First-row transition metals: (e) Dobbs, K. D.; Hehre, W. J. *Ibid.*, submitted for publication.

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Table I. Variations in CH, CC, CF, CSi, and CCl Bond Lengths with Hybridization at Carbon

molecule	hybridization at carbon	bond length^a 3-21G^b	bond length^a exptl^c
CH Bond			
ethane	sp^3	1.084	1.102^d
ethylene	sp^2	1.074 (−0.010)	1.085 (−0.017)
acetylene	sp	1.051 (−0.034)	1.061 (−0.041)
CC Bond			
propane	sp^3	1.541	1.526
propene	sp^2	1.510 (−0.031)	1.501 (−0.025)
propyne	sp	1.466 (−0.075)	1.459 (−0.051)
CF Bond			
fluoroethane	sp^3	1.410	1.398
fluoroethylene	sp^2	1.363 (−0.047)	1.347 (−0.051)
fluoroacetylene	sp	1.297 (−0.113)	1.279 (−0.119)
CSi Bond			
ethylsilane	sp^3	1.886	1.866^d
vinylsilane	sp^2	1.867 (−0.019)	1.853 (−0.018)
silylacetylene	sp	1.825 (−0.061)	1.826 (−0.040)
CCl Bond			
chloroethane	sp^3	1.819	1.788
chloroethylene	sp^2	1.746 (−0.073)	1.726 (−0.062)
chloroacetylene	sp	1.644 (−0.175)	1.637 (−0.151)

[a] Deviations from bond lengths to sp^3 hybridized centers are given in parentheses. [b] 3-21G$^{(*)}$ for molecules incorporating second-row elements. [c] Unless otherwise noted, experimental structural data from: Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619. [d] Callomon, J. H.; Hirota, E.; Kuchitsu, K.; Lafferty, W. J.; Maki, A. G.; Pote, C. S. *Structure Data on Free Polyatomic Molecules*; Springer-Verlag: Berlin, 1976; Landolt-Börnstein, New Series; Group II, Vol. 7.

Table II. Variations in TiH, TiC, TiF, TiCl, and TiCp Bond Lengths with Hybridization at Titanium

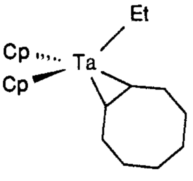
molecule	hybridization at titanium^a	bond length^b 3-21G (s only)^c	bond length^b 3-21G (sp)
TiH Bond			
$H_3Ti{-}CH_3$	sd^3	1.652	1.674
$H_2Ti{=}CH_2$	sd^2	1.714 (0.062)	1.754 (0.080)
$HTi{\equiv}CH^d$	sd	1.884 (0.232)	1.930 (0.256)
TiC Bond			
$(CH_3)_3Ti{-}CH_3$	sd^3	2.070	2.082
$(CH_3)_2Ti{=}CH_2$	sd^2	2.125 (0.055)	2.132 (0.050)
$CH_3(H)Ti{=}CH_2$	sd^2	2.107 (0.037)	2.115 (0.033)
$CH_3Ti{\equiv}CH^d$	sd	2.280 (0.210)	2.266 (0.184)
TiF Bond			
$F_3Ti{-}CH_3$	sd^3	1.717	1.729
$F(H_2)Ti{-}CH_3$	sd^3	1.712 (0.005)	1.730 (0.001)
$F_2Ti{=}CH_2$	sd^2	1.752 (0.035)	1.758 (0.029)
$F(H)\ Ti{=}CH_2$	sd^2	1.742 (0.025)	1.753 (0.024)
$FTi{\equiv}CH^d$	sd	1.890 (0.173)	1.841 (0.112)
TiCl Bond			
$Cl_3Ti{-}CH_3$	sd^3	2.209	2.226
$Cl_2Ti{=}CH_2$	sd^2	2.302 (0.093)	2.304 (0.078)
$Cl(H)Ti{=}CH_2$	sd^2	2.324 (0.115)	2.326 (0.100)
$ClTi{\equiv}CH^d$	sd	2.472 (0.263)	2.413 (0.187)
TiCp Bond^e			
$Cp(H)_2Ti{-}CH_3$	sd^3		2.096
$Cp(H)Ti{=}CH_2$	sd^2		2.105 (0.009)

[a] Ignoring possible contributions due to participation of valence p-type atomic orbitals on the metal. [b] Deviations from bond lengths to sd^3-hybridized centers are given in parentheses. [c] Valence, 4p-type, atomic orbitals removed from the titanium basis set. [d] Constrained to "linear" structures. Actual calculated equilibrium structures show distortion both at titanium and at the alkyne carbon. Dobbs, K. D.; Hehre, W. J., unpublished results. [e] Bond length quoted refers to the distance between the metal and the centroid of the cyclopentadienyl ring.

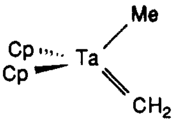
Metal–ligand-bonding molecular orbitals in organometallic compounds are made up primarily of (n) d- and ($n + 1$) s-type functions, where n is the principal quantum number. Valence ($n + 1$) p-type functions are usually assumed to play a lesser role. The d functions are less diffuse than the higher energy s- or p-type orbitals, and hybridization changes which lead to reduced d character should also result in an increase in metal–ligand σ-bond lengths, assuming that contributions due to valence p-type functions are small. Discounting p orbital contributions entirely, we note, for example, that changing from a tetrahedral, four-coordinate, to a planar-trigonal, three-coordinate, to a linear, two-coordinate geometry about a transition-metal center effects a change in hybridization from sd^3 to sd^2 to sd. This should lead to increased metal–ligand separation, the opposite trend as noted in analogous main-group compounds (cf. Table I). Such a suggestion is supported by calculated metal–ligand bond lengths in several related series of titanium alkyl, alkylidene, and alkylidyne complexes (Table II). Here all comparisons have been constructed to maintain the same formal electron count about titanium. Bonds to all substituents increase in length from the titanium alkyl to the analogous titanium alkylidene complexes and from alkylidene to the corresponding alkylidyne complexes. Even the cyclopentadienyl complexes appear to follow this trend, although the result here may well be fortuitous. Bonding of cyclopentadienyl to a transition metal involves several sets of orbitals and should be less sensitive to hybridization changes. Bond-length differences between alkyl and alkylidene complexes are generally of comparable magnitude to those previously noted between sp^3- and sp^2-hybridized carbon centers, although in a few cases they are significantly greater. Calculated bond-length increases from alkylidene to alkylidyne complexes are also generally larger than the bond-length shifts noted between sp^2- and sp-hybridized carbon centers.

Differences in structural parameters from 3-21G calculations on titanium compounds with and without 4p functions on the metal allow assessment of the role which these functions play in metal–ligand binding. As expected, metal–ligand bonds for all systems considered lengthen as a result of the addition of p functions. Not only are the effects small (0.01–0.04 Å), but they are also relatively uniform for different hybridization states. It would appear, therefore, that valence p-type orbitals are not of major influence in directing geometry changes with differing hybridization for the model systems dealt with here. Valence p-type orbitals may, however, become more important for organometallic systems in which the central metal is nearly or completely saturated.

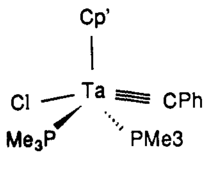
Experimental structural data on closely related complexes with which to test the simple hypothesis are scarce. Metal–cyclopentadienyl distances in the series of tantalum complexes



TaCp = 2.05 Å[5]



TaCp = 2.10 Å[6]



TaCp′ = 2.13 Å[7]
(Cp′ = η^5-C_5Me_5)

which, while differing in ligand types, maintain the formal electron count about tantalum, increase from the alkyl complex to the metal alkylidyne, in accord with the conclusions of the simple hybridization arguments.

In conclusion, molecular orbital calculations on simple organotitanium complexes suggest metal–ligand bond lengthening from the metal alkyl to the alkylidene and further lengthening from the alkylidene to the alkylidyne. This results from hybridization changes at the metal center; reduction in d-orbital character leads to an increase in metal–ligand bond length. The phenomenon is general and subject to widespread experimental test, although little data now in the literature may be brought to bear.